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APPLICATION OF UV-LED PHOTOCATALYSIS TO REMOVE VOCs FROM INDOOR AIR

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APPLICATION OF UV-LED PHOTOCATALYSIS TO REMOVE VOCsFROM INDOOR AIR

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ABSTRACT

Photocatalytic oxidation (PCO) using UVLED is a promising technology for indoor air purification. PCO destroys most organic contaminants at low concentrations at near-ambient temperatures. PCO needs a light energy sufficient to photoactivate semiconductor photocatalyst by supplying the catalyst's band gap energy, high surface area of photocatalyst, and an oxidizing agent such as O_2. The most commonly used photocatalyst, TiO_2 is excellent in breaking down wide variety of organic compounds. The minimal pressure drop, low power consumption, potentially long service life, and low maintenance are also additional factors which make PCO an efficient method for indoor air applications. Ultra Violet Light Emitting Diode (UVLED) is a new concept in the field of PCO which has several advantages over conventional UV light sources. Limited research has been conducted using UVLED PCO for air treatment. This study demonstrated the potential application of UVLED for the removal of VOCs (toluene and xylene) from indoor air under different operating conditions including flow rate, types of catalysts, LED intensity, and humidity. This study explored the feasibility of UVLED application in pilot scale room air cleaner.

Key Words: UVLED, PCO, Catalyst, Indoor Air Quality, VOCs

CO- AUTHORSHIP

This thesis was written in accordance with the guidelines and regulations for a format stipulated by the School of Graduate and Postdoctoral Studies at the University of Western Ontario. The candidate conducted all the laboratory experiments, analyzed and interpreted the laboratory data under a close guidance and supervision of Dr. Madhumita Ray.

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To the ultimate source of love, care and support

My dear family

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ABBREVIATION

APCVD	Atmospheric Vapor Chemical Vapor Deposition
BTEX	Benzene Toluene Ethylbenzene Xylene
CVD	Chemical Vapor Deposition
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
GC	Gas Chromatography
HEPA	High Efficiency Particulate Air
IAQ	Indoor Air Quality
MOCVD	Metal Organic Chemical Vapor Deposition
PCO	Photo Catalytic Oxidation
PCA	Photo Catalytic Activity
PET	Poly-Ethylene Terephthalate
PDDA	Poly Diallyl Dimethyl Ammonium
PSS	Poly Styrene Sulfonate
SEM	Scanning Electron Microscopy
TEAM	Total Exposure Assessment Methodology
UVLED	Ultra Violate Light Emitting Diode
VOC	Volatile Organic Compound
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

The indoor air quality is of immense concern, especially in public places such as schools, offices, shopping malls, etc. mostly due to tightly sealed buildings for energy conservation and in some cases due to poor ventilation. In cold climate, people spend most of their time indoors where diverse indoor air contaminants are present in trace level to very high concentrations. The utilization of synthetic building materials, modern office equipment (photocopiers, laser printers, and computers), furnishings, cooking and cleaning products, numerous personal care products as well as outdoor air pollution can contribute to a considerable amount of indoor air impurities. Indoor air pollutants mainly consist of particulates, chemical and microbial pollutants. Volatile organic compounds (VOCs) are among the most common chemical pollutants in the indoor air that we breathe (WHO, 1989; USEPA, 1990). According to Little et al., (1994); Meininghaus et al., (1999); Kim et al., (2001); Wang et al., (2007), some of these compounds are associated with sick building syndrome (SBS) including mucous membrane irritation, headache and fatigue; others are known carcinogens (e.g., formaldehyde, acrolein (OEHHA, 2007)). According to Fisk and Rosenfeld, (1997), millions of people are currently suffering from the consequences of poor indoor air quality and billions of dollars are lost in the world each year due to poor indoor air quality. As many as one billion people, mostly women and children, are regularly exposed to levels of indoor air pollution exceeding WHO guidelines by up to 100 times (press release WHO/56, 14 September 2000).

For the quick and economical removal of VOCs from indoor air, many advanced technologies have recently been developed. Among the various technologies that are available for the removal of VOCs from air, photocatalytic oxidation (PCO) is the most promising mainly due to its capability of complete mineralization of the organic pollutants (Tompkins, 2001). Most of the other very effective technologies such as filtration, adsorption simply transfer the pollutants from one phase to another.

Photocatalytic oxidation (PCO) using UV radiation has been widely used in the literature in both air and water phases for the removal of organics. While active UV photocatalytic oxidation (UVPCO) methods (Hoffmann et al. 1995, Pichat et al 2000, Ollis, 2000 and Hodgson et al. 2007) are more efficient, passive methods, in which volatile organic compounds (VOCs) react over irradiated indoor surfaces, have also been shown as promising pollution abatement technologies. In passive methods, the photocatalytic particles usually TiO_2 are supported on materials that must be strongly attached to building surfaces and/or to the air purifiers' hardware, resisting environmental aging and mechanical abrasion. Supports also should be chemically inert, or participate in the chemical process facilitating pollutant elimination, and various support materials for TiO_2 include glass, quartz, paper, cement, activated carbon fibers, ceramics, stainless steel, and polymeric matrices such as poly-ethylene terephthalate (PET) and cellulose acetate. Significant research efforts have been devoted to improve the photocatalytic efficiency of TiO_2-based nanoparticles through chemical and physical transformation. Such changes include doping with transition metal ions and nonmetallic elements as well as structural transformations at nano scale (Kibanova et al. 2009 and Bhattacharya et al. 2004). According to Bhattacharya et al. (2004), TiO_2 was impregnated

on three different kinds of adsorbents, mesoporous (MCM-41), microporous (b-zeolite) and pillared structure (montmorillonite) where different loadings (10–80%) of TiO_2 were obtained using sol–gel method. They reported that the supported catalysts effectively removed an azo-dye orange II from solution, and the rate of degradation was significantly better than that of bare TiO_2 (sol–gel) and Degussa-P25. They further reported that the performance improvement can be attributed to the high surface areas of the adsorbent used, crystallinity and particle size of deposited TiO_2.

Kibanova et al. (2009) demonstrated clay-supported TiO_2 photo catalysts could potentially increase the performance of air treatment technologies via enhanced adsorption and reactivity of target volatile organic compounds (VOCs). Both natural and synthetic clays are receiving increasing attention as supports of TiO_2-based photocatalysts for air and water remediation (Pichat et al.2005, Kun et al.2006, Ooka et al.2004 and Mogyorosi et al, .2003). Clays often present a large surface area for reversible and irreversible adsorption of organic contaminants. Embedding TiO_2 nanoparticles in clay matrices is expected to improve the photocatalytic efficiency by enhancing VOC retention through adsorption in clay pores. In addition, clays can also act as electron acceptors or donors (Solomon, 1968) and have the ability to catalyze diverse chemical processes such as polymerization, reduction, decomposition, or acid-base reactions (Solomon, 1968; Mingelgrin et al.1979 ; Fusi et al.1982; Ernstsen 1996).

Although, the most common light source for TiO_2 photocatalysis is the black-light-type UV lamp (Fujishima et al. (2005)), which emits light in the UV-A band (Δmax = 355 nm). However, the volume of the tube-type black light is relatively large, so that it cannot meet the

requirements of miniaturized photocatalytic devices. Light emission diodes (LED) that can emit ultraviolet light, generate spectral distribution at 370 and 400 nm of wavelengths well suited for activating anatase and rutile -type TiO_2, respectively. UVLED devices are almost ideal light sources for miniaturized photocatalytic devices. The light sources of UVLED (600 and 800 mW) can save significant amount of energy in comparison with the traditional UV lamps (12 and 16 W) and much safer with less UV intensity (Shie et al., 2008). In addition, UV-LEDs are durable, robust, small in size and high in efficiency, can be applied as the UV source during PCO (Chen et al. 2005). However, the application of UVLED in PCO is very new and has not been studied comprehensively.

1.2 OBJECTIVES OF THE STUDY

Light emission diodes (LED) that can produce ultraviolet light, make spectral distribution at 370 and 400 nm of wavelengths are well suited for activating anatase and rutile type TiO_2, respectively and UV-LEDs are robust as well as small in size and high in efficiency, can be used as the UV source during PCO. The objective of this study is to demonstrate the applicability of UV-LED in photo-catalytic oxidation of VOCs such as toluene, xylene. The photo-catalytic activity of several catalysts such as Degussa P25, nitrogen doped TiO_2 (TiO_2/N), Clay TiO_2, and a proprietary Bi_2O_3 catalyst was tested using UVLED in a continuous reactor treating 25-100 cfm of air spiked with the VOCs.

Based on the above, the objectives of the proposed work are

1) to develop a reactive air cleaning unit to remove volatile organic compounds using UVLED as light source.

2) to develop a titanium-dioxide (TiO_2), clay-TiO_2 and N doped TiO_2 catalyst system, which can be activated by common UV LED for the removal of volatile organic compounds such as toluene and xylene.

3) to characterize the performance of different catalysts under different conditions.

The proposed air cleaning device combined the above concepts. The concentration of the organics in the inlet and the outlet of the air cleaner was measured using an automatic gas sampling system connected with GC-FID (Gas Chromatography-Flame Ionization Detector).

1.3 CONTRIBUTION OF THE THESIS

In this study, catalysts (Degussa P25, solgel TiO_2, nitrogen doped TiO_2 (TiO_2/N), Clay TiO_2, and Bi_2O_3) were used in the reactor to characterize the removal performance of indoor air pollutants e.g. VOCs. This is one of the very few studies that have, to date, examined Toluene and Xylene removal from indoor air using these catalysts with UVLED in the continuous reactor. The intent is to develop an energy efficient and easily manufactured continuous reactor to remove VOCs from indoor air. The performance of the system was characterized with respect to air flow rate, humidity, types of catalysts, and light intensity.

1.4 ORGANIZATION OF THE THESIS

This thesis consists of five chapters and one appendix. Chapter 1 contains introduction, objectives as well as contribution of the thesis.

Chapter 2 discusses the literature review including indoor air quality (IAQ), toluene, toluene sources and concentrations in indoor environments; xylene; air cleaning devices; photo-catalysis and UVLED for photo-catalysis. Principles of reactor design is also discussed in this chapter.

Chapter 3 deals with materials and methods of this study. A brief description of catalyst preparation is also presented. Experimental setup is described in this chapter.

Chapter 4 discusses the experimental data analysis. Results showed that the VOCs removal was dependent on air flow rate, light intensity, and type of catalysts. Photolysis and photo-catalysis are described in this section.

Chapter 5 provides conclusions and recommendation for future studies and engineering application of the UVLED to reduce VOCs from indoor air.

The appendix contains the tables of results obtained from experimental analysis of VOCs at different conditions in the continuous reactor.

CHAPTER 2

LITERATURE REVIEW

2.1 INDOOR AIR QUALITY (IAQ)

IAQ is a term referring to the air quality within and around buildings and structures, especially as it relates to the health and comfort of building occupants. IAQ can be affected by microbial contaminants (mold, bacteria), gases (including carbon monoxide, radon, volatile organic compounds), particulates, or any mass or energy stressor that can induce adverse health conditions. Indoor air is becoming an increasingly more concerning health hazard than outdoor air. Using ventilation to dilute contaminants, filtration, and source control are the primary methods for improving indoor air quality in most buildings. Volatile organic compounds (VOCs) refers to organic chemical compounds which have high vapor pressures and which can affect the environment and human health.Volatile organic compounds (VOCs) are carbon and hydrogen-containing chemicals, which evaporate readily or are gases at room temperature and pressure and are important pollutants in indoor air (Yu et al., 2007; Wang et al., 2007). According to Wang et al. (2007), compared to outdoors, higher concentrations of VOCs can be found indoors where there is limited ventilation. The U.S. Environmental Protection Agency (EPA) Total Exposure Assessment Methodology (TEAM) studies expressed that indoor VOC levels were typically 2 to 5 times higher than outdoor concentrations (U.S. EPA, 2009; Birnie et al., 2006).

VOCs in indoor air can come from gaseous emissions of household chemicals and products (U.S. EPA, 2009). There are thousands of different VOCs produced and present in our daily lives (Minnesota Department of Health, 2009). These include those coming from cleaning and

degreasing agents, pesticides, air fresheners, toilet bowl deodorants, environmental tobacco smoke (second hand smoke), furniture and building materials (e.g. wood products, adhesives, carpeting, paints, varnishes, vinyl floors, moth balls, solvents, gasoline, newspaper, upholstery fabrics, sealing caulks), cosmetics, fuel oil, vehicle exhaust, cooking and photocopying (U.S. EPA, 2009; Minnesota Department of Health, 2009). Common VOCs include acetone, benzene, ethylene glycol, formaldehyde, methylene chloride, perchloroethylene, toluene, xylene, and 1, 3- butadiene. Acetaldehyde, a component of Environmental Tobacco Smoke (ETS), is one of the organic compounds that accumulates in rooms. Xu and Shiraishi (1999) and Tang et al. (2004) reported it as a key indoor air pollutant. Minnesota Department of Health (2009) listed a variety of factors that affect levels of VOCs in an indoor environment. These are volume of air in the room/building, the rate at which the VOC is off-gassed, the building ventilation rate, outdoor concentration, and the time spent by people in the affected environment. Among the various sources of VOCs mentioned above, building materials are considered to be the largest source of VOCs in indoor air (Wang et al., 2007). Thus, it is always expected that the concentration of VOCs in a new building will be higher than in old buildings. For instance, formaldehyde, a common VOC in mobile homes is found in many indoor products, such as pressed wood, paints, insulation, coated paper products, and combustible materials. Formaldehyde is responsible for indoor pollution because of its direct threat to people with their respiratory system. Further, together with benzene and toluene, they are the major contributors to the very harmful indoor air pollution. Therefore, formaldehyde release is subject to strict environmental regulations (Wang et al. 2007). They further reported that VOC concentrations indoors are typically in the ppb to sub-ppm range. However chronic exposures to low levels of these compounds can increase some people's risk of health

problems (Minnesota Department of Health, 2009). This is true for some people who have existing respiratory problems and higher sensitivity to chemicals. Many VOCs are toxic and considered to have carcinogenic, mutagenic or teratogenic effects (Alberici and Jardim, 1997) in both animals and humans. Long-term exposure to high concentrations of some VOCs can cause cancer and damage to vital organs of our body such as liver, kidney and central nervous system. Short term exposure to high concentrations of VOCs can cause eye, nose and throat irritation, headaches, nausea, vomiting, dizziness, fatigue, allergic skin reaction, and worsening of asthma symptoms (Minnesota Department of Health, 2009; U.S. EPA, 2009). VOCs are also considered one of the causes of Sick Building Syndrome (SBS). SBS is a situation in which the occupants experience acute and chronic effects that appear to be associated with the time spent in the building but no specific illness or cause can be determined (U.S. EPA, 2008). To eliminate SBS, building air must be cleaned or properly refreshed, and/or the sources of VOCs must be removed or modified. VOCs cannot be avoided, but indoor concentrations can be lowered by using materials and products with lower VOC emissions, proper ventilation and use of air purifiers. The presence of these compounds from a variety of sources represents a significant burden to indoor air environments. It is therefore necessary to apply control measures that would safeguard building occupants from exposure to these harmful compounds.

Table 2.1 Classes of VOCs and their possible emission sources (Cheng and Brown, 2003)

VOC class	**Environment source**
Aliphatic and cyclic hydrocarbons	1, 2, 4, 5, 7, 9–11
Aromatic hydrocarbons	1–7, 9, 11, 12
Aldehydes	1–12
Terpenes	1–4, 7–10
Alcohols	1–9, 11
Esters	1, 2, 4, 7–9
Halocarbons	1, 2, 7, 11
Glycols/glycolethers/glycolesters	1–4, 7, 9
Ketones	1–4, 6–12
Siloxanes	11
Alkene	2, 7
Organic acids	2, 3, 7–9, 11
Ethers	9
Other VOCs	1, 2, 4, 7, 11

Source: 1: Established buildings, 2: new and renovated buildings, 3: school, 4: new car interiors, 5: carpets, 6: floor coverings, 7: wood-based panel and furniture, 8: solid woods, 9: paints, 10: cleaning products, 11: unglued gas heaters and electric ovens, 12: office equipment.

Van Winkle and Scheff (2001) reported that toluene, together with benzene, ethyl benzene and xylene are grouped as BTEX compounds. BTEX is the major group found in indoor environments in different countries. Average indoor air concentration of toluene vary between 5 and 50 ppbv (Tilborghs et al. 2005), with maximum concentrations up to 9 ppm (AERIAS 2006).

2.2 TOLUENE

Toluene is a clear, colourless liquid with a sweet, pungent odour. It is produced commercially, primarily through the catalytic conversion of petroleum or recovered as a by-product of the coke oven industry. These chemicals are harmful to human health when inhaled for long periods. Toluene is cheap and most frequently used as a solvent for paints, printing ink and adhesives. It smells like gasoline. Toluene should not be inhaled due to its health effects. Low to moderate levels can cause tiredness, confusion, weakness, drunken-type actions, memory loss, nausea, loss of appetite, and hearing and color vision loss, at high levels it can also cause unconsciousness, and even death. These symptoms usually disappear when exposure is stopped. In controlled exposure studies, healthy adults exposed to toluene for 4.5 to 7 hours reported increased eye, nose, and throat irritation as well as headaches, dizziness or feelings of intoxication at concentrations ranging from 189 to 566 mg/m^3 (Andersen, Lundqvist and Molhave 1983; Baelum et al. 1990), but not at 38 or 151 mg/m^3 (Andersen, Lundqvist and Molhave 1983). Several occupational studies have reported effects of toluene on neurobehavioural endpoints (tests of manual dexterity, visual competency, and attention span) at concentrations ranging from 264 to 441 mg/m^3 (Foo et al. 1988; Foo et al. 1990; Boey et al. 1997; Eller et al. 1999; Kang et al. 2005). No effects were seen at concentrations ranging from

75 to 113 mg/m^3 (Kang et al. 2005), nor was any difference seen between exposed workers (98 mg/m^3) and a reference group (11 mg/ m^3) (Seeber et al. 2004; Seeber et al. 2005).

2.2.1. Toluene Sources and Concentrations in Indoor Environments

A review of toluene sources and concentrations has been published by the World Health Organization (World Health Organization, 1985). Exposure to toluene is generally via indoor air (Hodgson 2000; Kim, et al. 2001; Hodgson and Levin 2003; Won et al. 2005; Héroux et al. 2008). Indoor sources of toluene include building materials (e.g., solvent- and water-based adhesives, floor coverings, paint, chipboard), consumer and automotive products (e.g., cleaners, polishes, adhesive products, oils, greases, lubricants), and environmental tobacco smoke. In attached garages, toluene generated by running engines or by product storage may also infiltrate into the indoor environment. Canadians' exposure to toluene is attributed predominantly to indoor air, because indoor air levels generally exceed ambient air levels, and because of the greater time spent indoors. Median concentrations of toluene measured in Canadian residences range from 5.5 to 24.7 μg/m^3 (0.0055 to 0.0247 mg/m^3) and average concentrations from 11.5 to 34.4 μg/m^3 (0.0115 to 0.0344 mg/m^3) (Zhu et al. 2005; Héroux et al. 2008; Health Canada 2010b; Health Canada 2010c). Peak concentrations can reach values one to two orders of magnitude higher.

2.3 XYLENE

Xylene is a colourless liquid, with a strong, sweet odour. The term xylene refers to a mixture of three structural isomers of the aromatic hydrocarbon dimethylbenzene. The chemical has almost the same smell and usage as toluene. Xylene is used as a solvent, to manufacture petrol, as a raw material to manufacture chemicals used to make polyester fibre, and to make dyes, paints, lacquers, and insecticides. It is used to sterilise some materials. Xylenes are common in domestic products such as aerosol paints, architectural coatings, automobile and machinery paints and primers, caulks, insecticides and fungicides for yards and gardens, hard surface cleaners, lubricating oils, markers, automotive chemicals, paints and varnish, paint and varnish removers and thinners, pet flea and tick products, pesticides, shoe polish, interior clear finishes, undercoats, and primers, sealants, resin and rubber adhesives, waterproofing compounds, and wood office furniture. Since xylene is used in many consumer products, short-term indoor concentrations may be elevated above the levels considered safe for workers. Workers in the industries that use or produce xylene are at risk of exposure. Consumers can also be exposed to xylene by exposure to air from production and processing facilities that use xylene. When xylene is released to the water or soil, it will evaporate rapidly; exposure from contaminated water is therefore unlikely.

Xylene enters the body by the inhalation of contaminated air, and liquid xylene can be absorbed through the skin. Xylene may irritate the skin, eyes, nose and throat, may cause stomach problems, drowsiness, loss of memory, poor concentration, nausea, vomiting, abdominal pain and incoordination. High levels may cause dizziness, passing out, and death. Repeated exposures may damage bone marrow, which causes a low blood cell count. Xylenes

may damage a developing foetus. Xylene exhibits neurological effects. High levels from exposure for acute (14 days or less) or chronic periods (more than 1 year) can cause headaches, lack of muscle coordination, dizziness, confusion, and alterations in body balance. Exposure of people to high levels of xylene for short periods can also cause irritation of the skin, eyes, nose, and throat, difficulty in breathing and other problems with the lungs, delayed reaction time, memory difficulties, stomach discomfort, and possibly adverse effects on the liver and kidneys. It can cause unconsciousness and even death at very high levels. Xylene or products containing Xylene should not be used indoors or around food.

2.4 AIR CLEANING DEVICES

Air cleaning devices are used to supplement source control and ventilation in reducing and maintaining acceptable levels of indoor air contaminants. Air cleaning devices alone cannot ensure adequate air quality, particularly where significant sources are present and ventilation is inadequate. Air cleaners are classified according to their specific purposes. The type of device should be selected according to the governing cleaning mechanism. Thus, a particulate control device is different from the devices for gaseous pollutants.

The three general types of air cleaners for particulate removal are mechanical filters, electronic air cleaners, and ion generators (U.S. EPA, 2007). Mechanical filters can be installed in ducts in homes and buildings with central heating and/or air-conditioning or may be used in portable devices which contain a fan to force air through the filter. Mechanical filters can be in the form of flat or panel filters, pleated or extended surface filters, or high efficiency particulate air (HEPA) filters. Flat or panel filters can be made of low packing density of coarse glass fibers,

animal hair, or vegetable fibers often coated with a viscous substance (U.S. EPA, 2007). Electronic air cleaners utilize an electrical field to catch charged particles. They can be installed in central heating and/or air conditioning system ducts or in portable units with fans. Some of the most common electronic air cleaners are electrostatic precipitators or charged-media filters. Electrostatic precipitators collect particles on a series of flat plates while in charged media filters, particles are collected on the fibers. To attain higher collection efficiency, the particles are ionized or charged prior to collection. Ion generators, like electronic air cleaners use static charges to remove particles from indoor air, except that they come in portable units only. The charging of the particles in the room attracts them to the walls, floors, table tops, draperies, occupants, etc. These devices come with a collector which attracts the charged particles back to the unit. Hybrid devices contain two or more of the particle removal systems discussed above. For instance, one or more types of mechanical filters may be combined with an electrostatic precipitator or an ion generator.

There are limited number of studies on the effectiveness of portable or residential air cleaners in removing gaseous pollutants. Adsorbents and/or reactive adsorbents can be used with particle removal devices for removing gaseous pollutants in indoor air. This is due to the fact that gaseous pollutants cannot be removed by air cleaning devices that are based on filtration and electrostatic attraction alone. The performance of solid sorbents used with these systems depends on the following (U.S. EPA, 2007):

I. Air flow rate through the sorbent bed

II. Concentration of the pollutants

III. Presence of other gases or vapors

IV. Physical and chemical characteristics of the pollutants and the sorbent

V. Configuration of the sorbent in the device

VI. Quantity of sorbent used and the sorbent bed depth

Generally, the efficiency of the above system decreases with the amount of pollutant captured and is usually rated by sorption capacity and penetration time. The most common adsorbent material is activated carbon. It can adsorb some pollutants, mostly hydrocarbons and non-polar gases (Chin et al., 2006), even in humid conditions. One of the constraints of this type of adsorbent is that it is not efficient in adsorbing volatile, low molecular weight gases. In most cases, activated carbon is good in removing odor; however, the absence of odor alone does not guarantee good air quality. Zeolites are adsorbents that can be used for treating polar gases and vapors such as benzene, n-hexane and CH_2O from indoor air (Chin et al., 2006). At present, limited data are available on the effectiveness of this system in the removal of the low concentration range of pollutants typically found in an indoor air environment. One of the major concerns in this type of device is the useful capacity of the adsorbent as their lifetime can be short depending on the type and concentration of pollutant to be adsorbed. Other than carbon, there are also special sorbents available to treat specific pollutants, such as chemisorbents impregnated with chemically active materials to remove specific reactive gaseous materials.

US EPA (2008) reported that some air cleaners use ultraviolet (UV) light technology intended to destroy pollutants in indoor air. These air cleaners are called ultraviolet germicidal irradiation (UVGI) cleaners and photocatalytic oxidation (PCO) cleaners. Ozone is a lung

irritant that can cause adverse health effects. UVGI cleaners use ultraviolet radiation from UV lamps that may destroy biological pollutants such as viruses, bacteria, allergens, and molds that are airborne or growing on HVAC surfaces (e.g., found on cooling coils, drain pans, or ductwork). If used, they should be applied with, but not as a replacement for, filtration systems.

PCO cleaners use a UV lamp along with photocatalyst that reacts with the light. They are intended to destroy gaseous pollutants by converting them into harmless products, but are not designed to remove particulate pollutants. Ozone generators use UV light or an electrical discharge to produce ozone. Ozone is a lung irritant that can cause adverse health effects. At concentrations that do not exceed public health standards, ozone has little effect in removing most indoor air contaminants. Thus, ozone generators are not always safe and effective in controlling indoor air pollutants. Consumers should instead use methods proven to be both safe and effective to reduce pollutant concentrations, which include eliminating or controlling pollutant sources and increasing outdoor air ventilation.

One of the most promising techniques in indoor air cleaning that is still under development is the use of the photocatalytic oxidation (PCO) process. Considerable research has been devoted to improve the technology and extend its application for specific purposes. However, most of the studies have been performed under laboratory conditions. Photocatalytic reactions are useful for the treatment of air polluted with volatile organic compounds (VOCs) (Fu et al. 1996; Hoffmann et al. 1995). Hitherto, many researchers have investigated the photo-oxidation of VOCs and have reported that a variety of compounds, including hydrocarbons, alcohols,

chlorohydrocarbons and amines in gas phase are decomposed on the UV-irradiated TiO_2 under ambient conditions. Photocatalytic reactions have an advantage over other reactions, such as thermal incineration and catalytic incineration in that they can efficiently decompose low concentrations of VOCs under mild conditions. It has been reported, however, that TiO_2 catalyst is generally deactivated during the course of the VOC photooxidation (Sauer et al. 1996 ; Dibble et al. 1992).

Photocatalytic oxidation (PCO) by employing UV radiation is a promising approach of removing VOCs. When semiconductor materials such as titanium dioxide (TiO_2) are illuminated by photons having greater energy than their band-gap energies, the material absorbs the photons. The electrons in the valence band of the material are excited into the conduction band which leaves electron holes in the valence band. The components of this activated pair, when transferred across the interface, are capable of reducing and oxidizing a surface-adsorbed organic compound. Studies have shown that gas–solid photocatalysis can decompose a wide variety of VOCs, including acetone, toluene, formaldehyde and benzene. All the intermediates and by-products of the reactions are oxidized to CO_2 and water vapor which are not harmful to people (Tompkins, 2001). Although many researchers have worked on PCO of VOC (Tompkins, 2001; Obee and Brown, 1995; Dreyer et al., 1997; Tao et al., 1997; Obee, 1996; Yoneyama and Torimoto, 2000), more work is needed to accurately model PCO reactors.

2.5 PHOTOCATALYSIS

Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalysed photolysis, light is absorbed by an adsorbed substrate. In photogenerated catalysis, the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (hydroxyl radicals, OH) able to undergo secondary reactions. Photocatalytic oxidation (PCO), or heterogeneous photocatalysis, is carried out when a semiconductor photocatalyst is irradiated by a light photon that has energy higher than the photocatalyst's band gap energy. In the case of titanium dioxide (TiO_2), a wavelength less than 385 nm is sufficient to exceed its band gap energy of 3.2 eV. When this happens, electron is promoted from the valence band to the conduction band leaving a hole in the valence band. The valence band hole and the electron in the conduction band react with water and oxygen (O_2) present in the surrounding air. As a consequence, two very potent oxidants, hydroxyl radicals (•OH) and super oxide ions are produced (Frazer, 2001; Jacoby et al., 1996; Maness et al., 1999). Hydroxyl radicals are highly reactive and non-selective oxidizers that can attack organic materials, including those that make up living cells. The valence-band hole and conduction-band electron can recombine in the bulk material and on the surface.

Several steps are involved in photochemical mechanisms in solid semiconductors. These steps are described in detail by Delasa et al. (2005) and Tompkins et al. (2005a), and presented briefly in the following section.

$$TiO_2 \xrightarrow{h\nu} TiO_2^*(e_{CB}^- + h_{VB}^+) \quad \textbf{(2-1)}$$

$$TiO_2^*(e_{CB}^- + h_{VB}^+) \xrightarrow{recombination} TiO_2 + heat \quad \textbf{(2-2)}$$

Production of hydroxyl radicals

$$H_2O_{ads} \rightarrow OH_{ads}^- + H_{ads}^+ \quad \textbf{(2-3)}$$

$$h_{VB}^+ + OH^- \rightarrow {}^\bullet OH \qquad \text{(oxidative reaction)} \quad \textbf{(2-4)}$$

Production of super-oxide

$$e_{CB}^- + O_2 \rightarrow O_2^{\bullet -} \qquad \text{(reductive reaction)} \quad \textbf{(2-5)}$$

$${}^\bullet OH + \text{Organic Reactants} + O_2 \rightarrow \text{Products}\,(CO_2, H_2O, etc.) \quad \textbf{(2-6)}$$

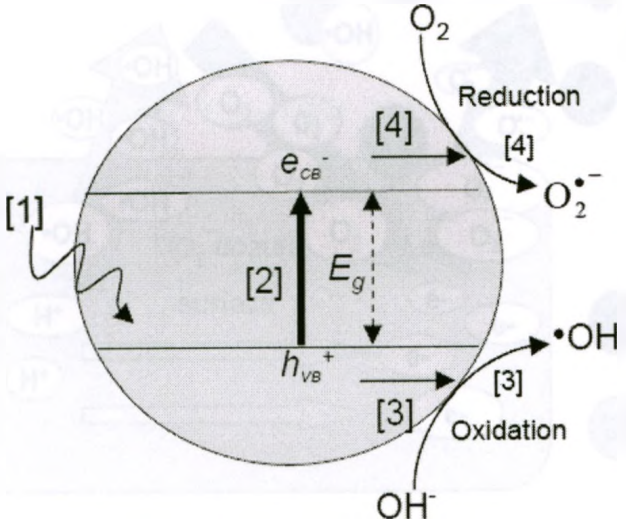


Figure 2.1: Steps of photochemical mechanisms in a solid semiconductor (Bayless, 2000):

[1] Light energy photon (hv) greater than band gap energy, Eg (3.2 eV for TiO_2); [2] excites electron from valence band to conduction band leaving a hole in the conduction band; [3] valence-band hole that successfully migrates to surface initiates oxidation reaction; [4] conduction-band electron that successfully migrates to surface initiates reduction reaction.

Hydroxyl radicals and superoxide ions produced from steps [3] and [4] can attack any organic compound (S) in the air that comes into contact with them to a more oxidized form, OS (see Figure 2.2).

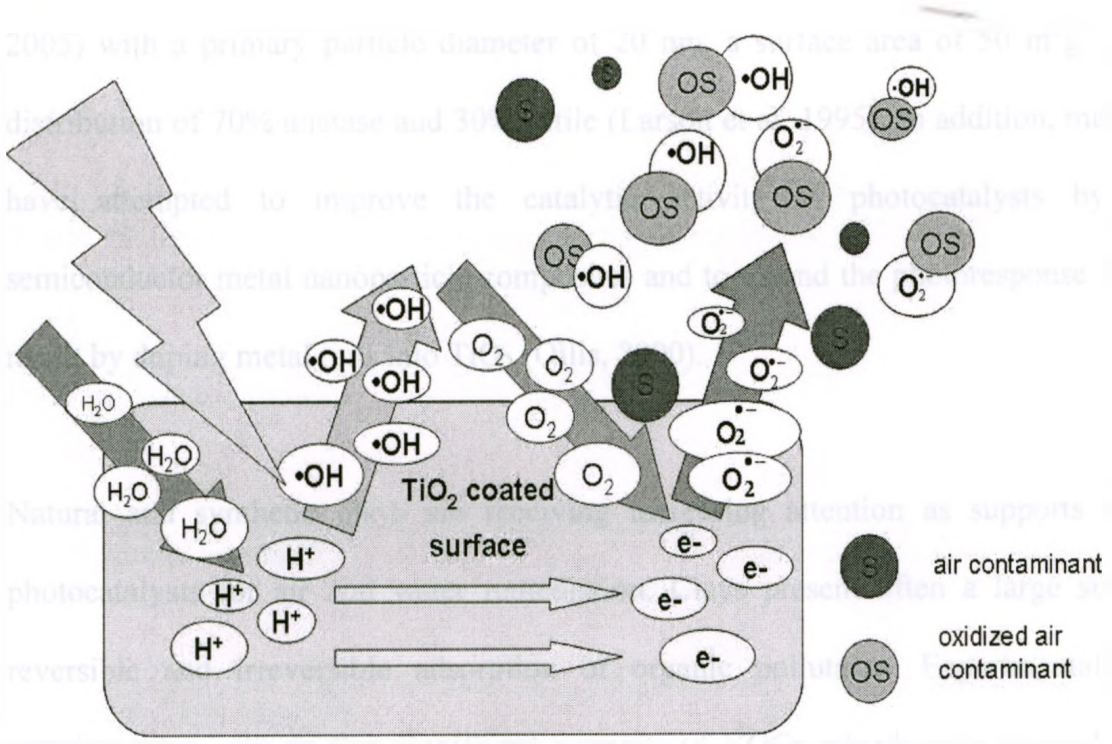


Figure 2.2: Photocatalytic destruction of organic compounds (Bayless, 2000).

The common photocatalysts are primarily metal oxides or sulphides, i.e., TiO_2, ZnO, ZrO_2, SnO_2, WO_3, CeO_2, Fe_2O_3, Al_2O_3, ZnS and CdS (Hoffmann et al., 1995). The most popular

choices of photocatalysts are TiO_2 and ZnO. Teichner et al. (Ollis, 2000) explored the photoactivity of numerous oxides for hydrocarbon partial oxidation in the gas phase, finding that the active catalysts involving titania, zinc, and tungsten ranked in the activity sequence: TiO_2 (anatase) > ZnO > WO_3. Much of the published work on photocatalysis uses TiO_2 as it is relatively inexpensive, stable chemically, and the photogenerated holes are highly oxidizing (Fujishima and Zhang, 2006).

TiO_2 has two crystal forms: anatase and rutile. The energy band-gaps of anatase and rutile are 3.23 and 3.02 eV, respectively. The commercial Degussa P25 prepared by flame pyrolysis (Maira et al., 2000) was used widely in air purification (Larson et al.1995; Kirchnerova et al. 2005) with a primary particle diameter of 20 nm, a surface area of 50 m^2g^{-1}, and a crystal distribution of 70% anatase and 30% rutile (Larson et al. 1995). In addition, many researchers have attempted to improve the catalytic activity of photocatalysts by synthesizing semiconductor metal nanoparticle composites and to extend the photoresponse into the visible range by doping metal ions into TiO_2 (Ollis, 2000).

Natural and synthetic clays are receiving increasing attention as supports of TiO_2-based photocatalysts for air and water remediation. Clays present often a large surface area for reversible and irreversible adsorption of organic pollutants. Experimentally determined sorption rates indicate that significant amounts of VOCs adsorb onto internal clay surfaces, with inter-particle and intra-particle diffusional time constants spanning two orders of magnitude). Embedding TiO_2 nanoparticles in clay matrices is expected to improve the photocatalytic performance by enhancing VOC retention through adsorption in clay pores. In

addition, clays can also act as electron acceptors or donors and have the ability to catalyze diverse chemical processes such as polymerization, reduction, decomposition or acid-base reactions. Synthesis of TiO_2 nanoparticles embedded in the structure of porous clays avoids the formation of macroscopic aggregates of photoactive particles that may lead to reduced efficiency. Furthermore, clays are stable supports that protect the TiO_2 particles from erosion or washing, and are inexpensive, non-toxic materials (Kibanova et al., 2009). According Puttamraju et al. (2008), photocatalytic degradation of Methyl Ethyl Ketone (MEK) was carried out in gas phase using TiO_2 supported on montmorillonite, β-zeolite and MCM-41 and resuts showed that The removal rates of MEK were higher for the catalysts supported on the adsorbent as compared to bare TiO_2 (Degussa P25 and sol-gel TiO_2) due to both improved adsorption and photocatalytic degradation.

Table 2.2 Summary of various photocatalysts (Mo et al. 2009).

Catalyst composition	**Preparation/coating method**
Commercial Degussa P25	Dip-coating
Other pure TiO_2 catalysts TiO_2	Sol–gel Sol–gel
Visible light responsive photocatalyst N-doped TiO_2	Sputtering Hydrothermal

	CVD APCVD MOCV
Synthetical composites with metal Metal ion TiO_2 $Pd–TiO_2$ $Ln^{3+}–TiO_2$	Sol–gel Hydrothermal and sintering Sol–gel
Synthetical composites with adsorption materials $TiO_2/SiO_2/ZrO_2$ TiO_2/SiO_2	Sol–gel Hydrothermal
Hybrid photocatalysts TiO_2 with ZnO, Al_2O_3, SiO_2, mordenite, and AC Mesoporous (MCM-41), montmorillonite, β-zeolite TiO_2+AC ZnO + AC	Sol–gel Stirring

Notes: CVD: chemical vapor deposition; MPCVD: metal-organic CVD; APCVD: atmospheric pressure CVD.

2.6 UV-LED FOR PHOTOCATALYSIS

The UV-light irradiation plays a potent energy provider on the photodegradation of VOCs. The activity of the photocatalyst depends strongly on the light-illumination (energy per unit area) or the photon flux on the surface of the catalyst. UV lamp has been commonly used for the applications of photocatalysis. The types of light sources used include Xe arc (300–800 nm), Hg–arc, Hg–Xe, and black-light lamp (6 W/GE, 100 W/UVP, 4 W/GEF4T5-BLB, 8 W/Sankyo Denki F8T8) (Shie et al., 2008). The most significant difference is that more intermediates are evolved by using the germicidal source, such as UV light, than those by using the black light (Zhao et al., 2003). However the traditional UV lamp has disadvantages of a short life, instability of the output power and the hazardous materials from the emitted wastes. The application of UV should be handled with care because the UV emission contains harmful light to humans. On the contrary, Ultra Violet Light Emitting Diode (UVLED) has a longer life with low electricity consumption and a higher reliability. The application of UVLED for photocatalysis is in its growing stage. Chen et al. (2005) first used the UVLED in the PCO of perchlororothylene (PCE). The authors used Degussa p25 as a catalyst and UV light output of $49 mW cm^{-2}$. The designed reactor delivered conversion of PCE up to 43%. According to their work, UVLED is an energy efficient solid state light source compared to other traditional light sources. Filament lamps are very inefficient sources of UV radiation and the inner space of gas discharge sources (fluroscent lamp and germicidial lamp) is filled with gas such as mercury vapour. While mercury can only meet all the requirement of the filling gas, it is harmful to health. On the other hand UVLED does not contain mercury, yet it emits radiation at 365 nm, useful for activating TiO_2 . Shie et al.(2007) showed the feasibility of UVLED

instead of traditional UV lamp to treat the formaldehyde using silver titanium oxide catalysts where concentration of formaldehyde decreasesd by 66 % relative to the initial concentration by using 40 LED (each 20 mW).

LED has more potential due to lower power and electromotive force (emf) demand, higher efficiency, life-span and security as compared to UV lamp. Also it does not generate heat. The light sources of UVLED can save a lot of energy in comparison with the traditional UV lamps. Although, the concept of photocatalysis using UVLED is proven by Chen at al. (2005) and Shie at al., (2007), further comprehensive studies involving pilot scale continuous reactor systems with variety of organics are required for full scale application of this technology.

2.7 PRINCIPLES OF REACTOR DESIGN

According to Birnie et al. (2006), the major elements required for the PCO process are combined to form a unit, within which the pollutants are neutralized. The aim of the reactor design is to obtain the greatest reaction yield, i.e. neutralize as much pollutants as possible, whilst expending the least amount of energy. To achieve this, reactor should provide effective contact among catalyst, reactants, and photons. They reported that for the catalyst to be effective it must have a high surface area, to allow contact with as large a volume of reactants as possible. Extremely large surface areas are possible when using powder form TiO_2. However, the need to immobilize TiO_2 on to a substrate results in a significant reduction of surface area. Unless sunlight is used, due to electricity charges and bulb replacement, the light source will tend to be the most costly component of any photo-reactor. Since photons are

expensive, it is essential to utilize them effectively and ensure that few are emitted that do not contact the catalyst and initiate oxidation. They further reported that efforts must be made to ensure that all reactor surfaces receive adequate irradiation from the light source, so that no flow paths through the reactor exist where the catalyst is not illuminated. Effective design is therefore essential to maximize surface area when using immobilized TiO_2, and to ensure that it is properly irradiated. The method of immobilization also demands careful consideration to ensure an adequate coating on the substrate surface.

CHAPTER 3
MATERIALS AND METHODS

3.1 MATERIALS

In this study, toluene and xylene with more than 99.5% purity were purchased from Claedon Chemicals Canada. Titanium tetra iso propoxide with more than 97% purity was obtained from Sigma Aldrich and sodium bentonite (clay) was purchased from Ywo Ben Inc, USA. Poly diallyl dimethyl ammonium (PDDA) contained 20 wt. % solution in water (average MW 200,000 - 350,000), poly sodium 4-styrene sulfonate (PSS) (30 wt. % solution in water, M_w=70,000) were purchased from Sigma Aldrich. In this research, TiO_2 Degussa P25 nanoparticles were obtained from Degussa, Germany with average diameter of 20 nm. N-doped TiO_2 and Bi_2O_3 were obtained from Vive Nano, Ontario, Canada. Analytical grade methanol, ehanol and acetone were purchased from Caledon Laboratories LTD (Ontario, Canada).

3.2 EXPERIMENTAL SET-UP

The experiments were conducted in a continuous flow reactor. The schematic diagrams of the experimental setup are shown in Figure 3.1 and 3.2. The indoor air purification device mainly consists of two components: the photo catalytic reactor and the gas buffer tank. In this study, the gas buffer tank with a volume of 200 gallon was used to mix the VOCs with incoming purified air to obtain a concentration range of 4 to 15 ppm of VOCs in the inlet of the reactor. Air flow rate in the system was varied from 25-117 cfm during the experiments. The photo-

reactor was supplied by Nutech Group of Industries, London, ON, Canada and is made of mild steel with a volume of 0.1054 m^3 or 26.37 gallons and consists of a catalyst coated screen with 60-120 UV light emitting diodes (LED) mounted on a perforated aluminum sheet. Wire mesh was used for catalyst's coating in the reactor and area of the mesh was 12" * 12" obtained from Mc-Master -carr supply company, Canada. Several photocatalysts were tested such as Degussa P25, clay-TiO_2, nitrogen doped TiO_2 and Bi_2O_3. UVLED used in the reactor generated a combined power of 72000 μWatt or 0.72 Watt at 360 nm.

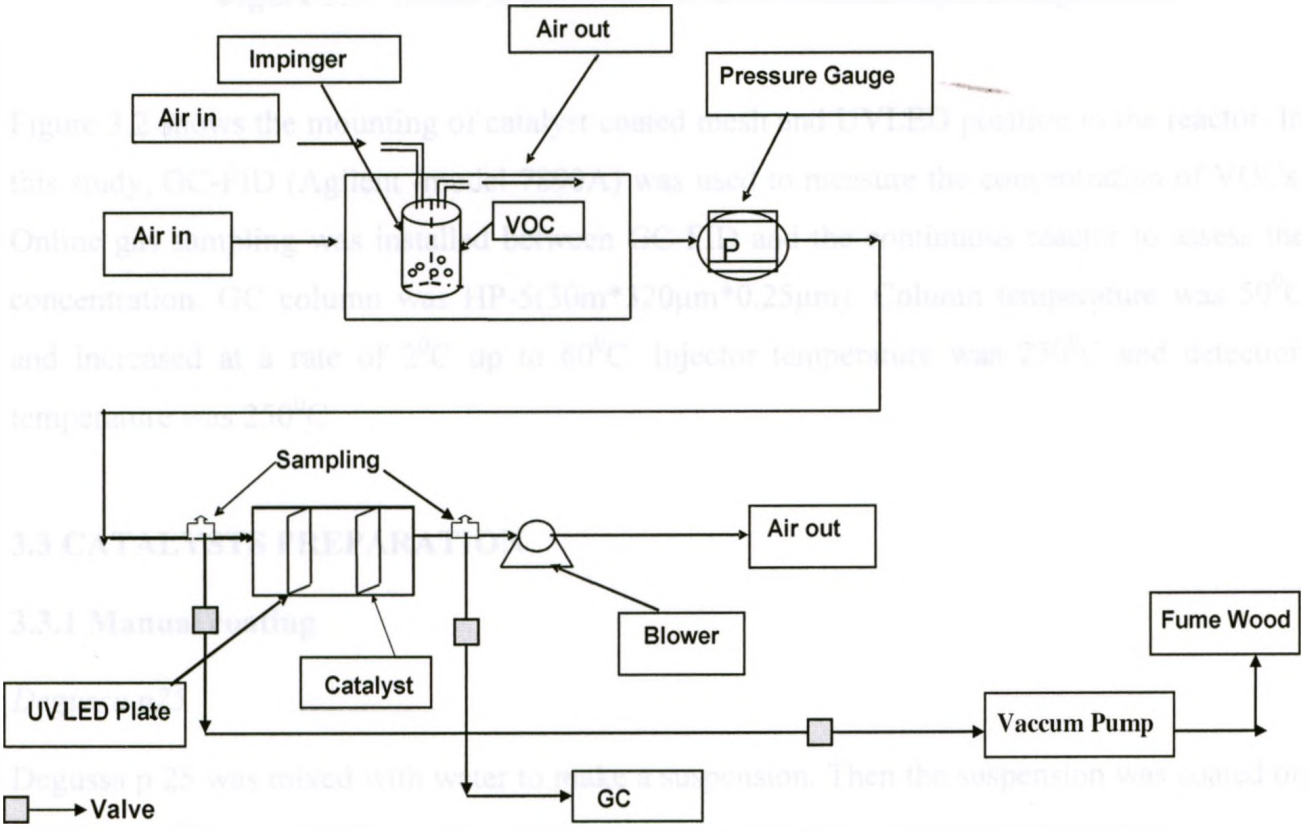


Figure 3.1 Experimental setup

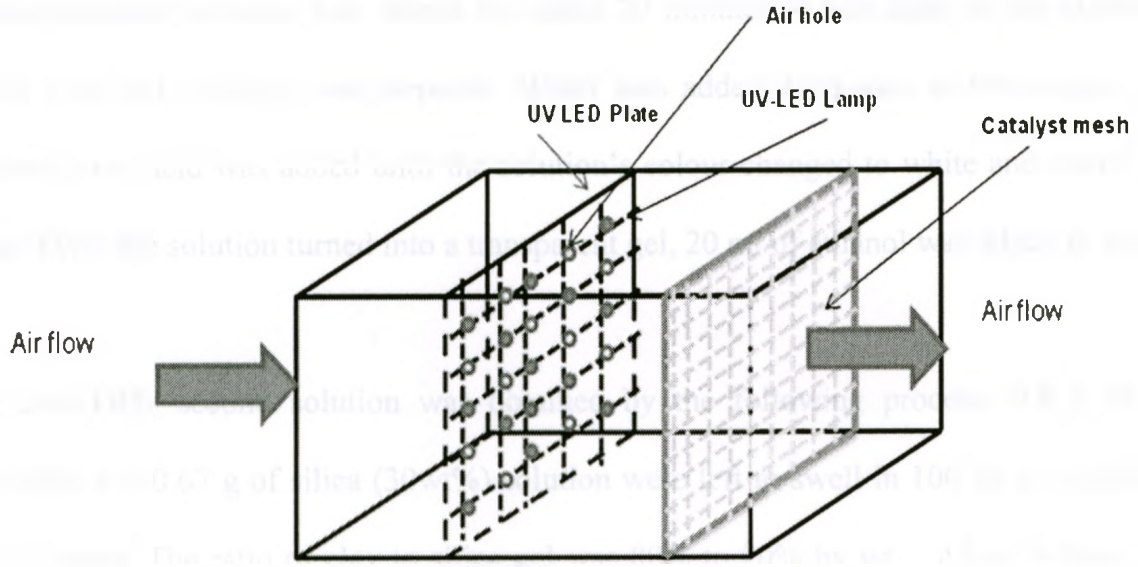


Figure 3.2: Inside of the reactor with LED and catalyst arrangement

Figure 3.2 shows the mounting of catalyst coated mesh and UVLED position in the reactor. In this study, GC-FID (Agilent -model 7890A) was used to measure the concentration of VOCs. Online gas sampling was installed between GC-FID and the continuous reactor to assess the concentration. GC column was HP-5(30m*320μm*0.25μm). Column temperature was 50^0C and increased at a rate of 2^0C up to 60^0C. Injector temperature was 250^0C and detection temperature was 250^0C.

3.3 CATALYSTS PREPARATION

3.3.1 Manual coating

Degussa p25

Degussa p 25 was mixed with water to make a suspension. Then the suspension was coated on the mesh with a brush. After coating, the mesh was kept in air to dry for overnight.

Clay-TiO_2

The sol gel method was used to prepare clay-TiO_2 catalyst. In this experiment, 2.4 ml of titanium tetra-iso-propoxide was added with 20 ml of ethanol. The ethanol and titanium

tetraispropoxide solution was stirred for about 20 minutes. It was kept on the stirrer for the entire time until sol-gel was prepared. Water was added drop-wise to the sol-gel solution. Hydrochloric acid was added until the solution's colour changed to white and then it became clear. Once the solution turned into a transparent gel, 20 ml of ethanol was added to the gel.

For clay-TiO_2, second solution was obtained by the following process: 0.8 g of sodium bentonite and 0.67 g of silica (30wt%) solution were left to swell in 100 ml of distilled water for 24 hours. The ratio of clay to silica gel was 80% to 20% by wt. After 24 hour, 1 mmol (0.169 g) of silver nitrate was added to swollen clay suspension. The volume of the mixture was brought to 500 ml by adding distilled water. Sol-gel diluted with ethanol prepared by above method was then added to the clay solution. The mixture of clay solution and sol-gel was then stirred for 24 hours. The solution was centrifuged at 3800 rpm and the temperature was kept at 25°C for 30 minutes. The clay settled at the bottom of the centrifuge was used to coat the wire mesh. The coated wire mesh was kept in an oven at 92°C for overnight. The dried wire mesh was then placed in a furnace for about 10 hours at 450°C. The catalyst was ready to be used for photo catalysis.

Sol-gel-TiO_2

10 mL of glacial acetic acid was mixed with 90 mL of de-ionized water at room temperature to obtain solution (A). 0.1 mol titanium iso-propoxide was dissolved in 100 mL of anhydrous ethanol with constant stirring to form solution (B). Then, the solution B was added drop-wise into the solution A within 60 min under vigorous stirring. Subsequently, the obtained sol was

stirred continuously for 2 h and coated on mesh and after coating, the mesh was kept at 90 °C for 6 hrs and finally mesh was calcined at 600°C for 4 hrs.

3.3.2 Dip coating

Dip coating was used in the preparation of Degussa P25, N-doped TiO_2 and Bi_2O_3 catalysts coated meshs. The mesh was cleaned by using warm water and detergent. Acetone, followed by distilled water was used to clean the mesh. After cleaning, the mesh was dried in air. The clean mesh was first deposited with a precursor layer of (PDDA/PSS) using 3 by 3 cycles of alternate immersion of the mesh in aqueous solutions of PDDA (1.0 mg ml^{-1}) and PSS (1.0 mg ml^{-1}) for 5 min, with intermediate water rinsing and air drying. The deposition of the precursor layer promoted the adhesion of the subsequently deposited nanoparticle films. Then the mesh were alternatively dipped in P25 TiO_2 (Degussa) aqueous solution (1.0 mg ml^{-1}, pH 3.0) and PSS aqueous suspension (1mg ml^{-1}) for 5 min, with intermediate water rinsing and air drying. By repeating the deposition process of TiO_2 and PSS layers in a cyclic fashion, multilayer films of (TiO_2/PSS)*n was achieved, where n represents the number of deposition cycles. The as-prepared coatings were calcined at 500 ° C for 1h to remove the organic part of the film. The similar procedure was followed for the preparation of N-doped TiO_2 and Bi_2O_3 coated mesh. Figure 3.3, 3.4, 3.5 show scanning electron microscopy (SEM) of Degussa P25, Bi_2O_3 and N-doped TiO_2 coated mesh using Dip coating.

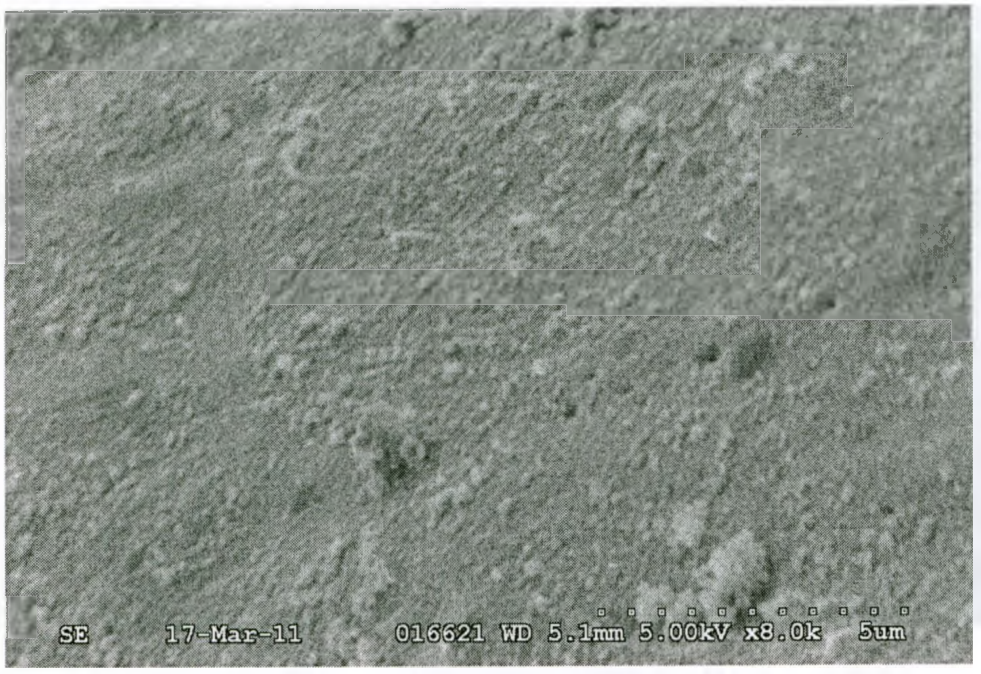


Figure 3.3: Scanning Electron Microscopy (SEM) of Degussa P25 coated mesh (Dip coating)

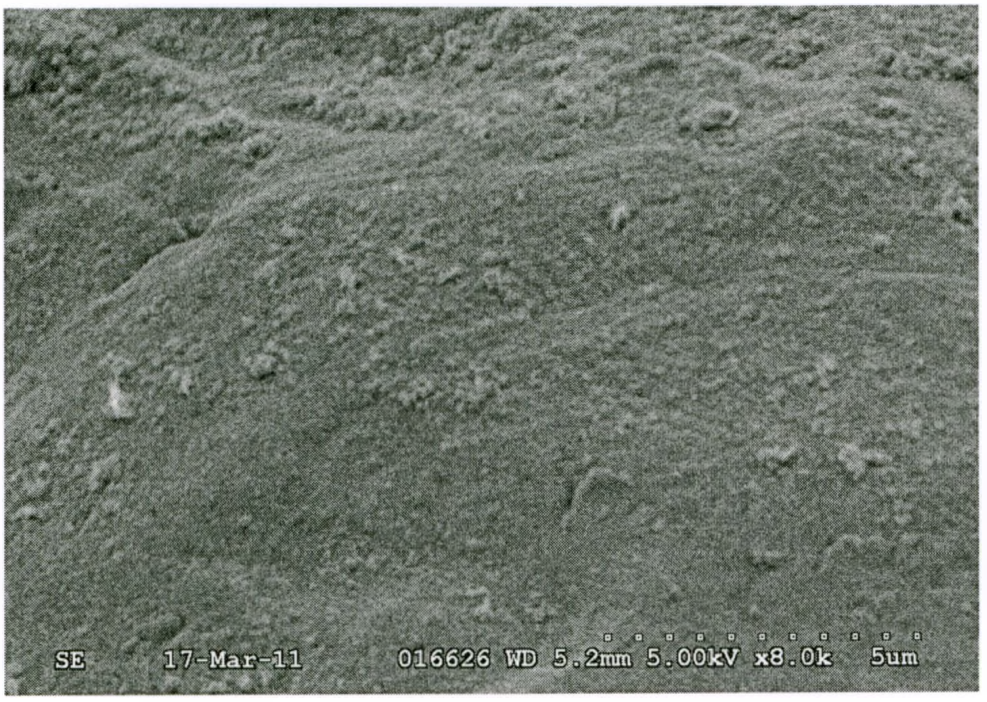


Figure 3.4: Scanning Electron Microscopy (SEM) of Bi_2O_3 coated mesh (Dip coating)

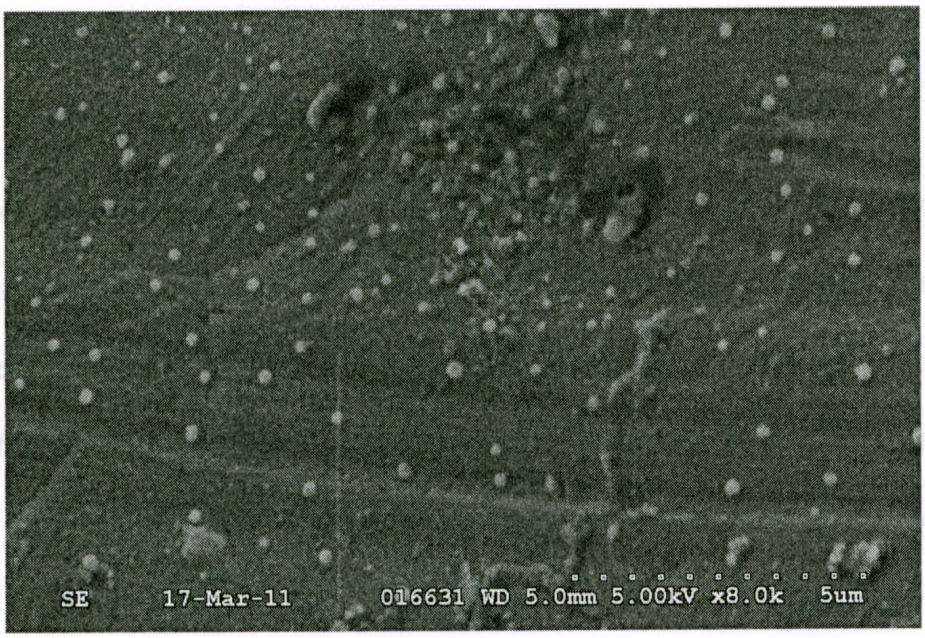


Figure 3.5: Scanning Electron Microscopy (SEM) of N-doped TiO_2 coated mesh (Dip coating)

CHAPTER 4

RESULTS AND DISCUSSION

The use of UVLED as a light source for photocatalysis of VOCs such as toluene and xylene in gas phase was evaluated in this study. The concentration of toluene and xylene in the experiments varied from 4-15 ppm. A series of experiments was conducted to evaluate the effect of important parameters such as type of catalysts, flow rate, type of coating, light intensity and relative humidity for the removal efficiencies of toluene and xylene. Five types of catalysts were used in the experiments namely Degussa p25, Clay supported TiO_2, Solgel-TiO_2, N-doped TiO_2 and Bi_2O_3. The flow rate was varied from 25 cfm to 117 cfm.

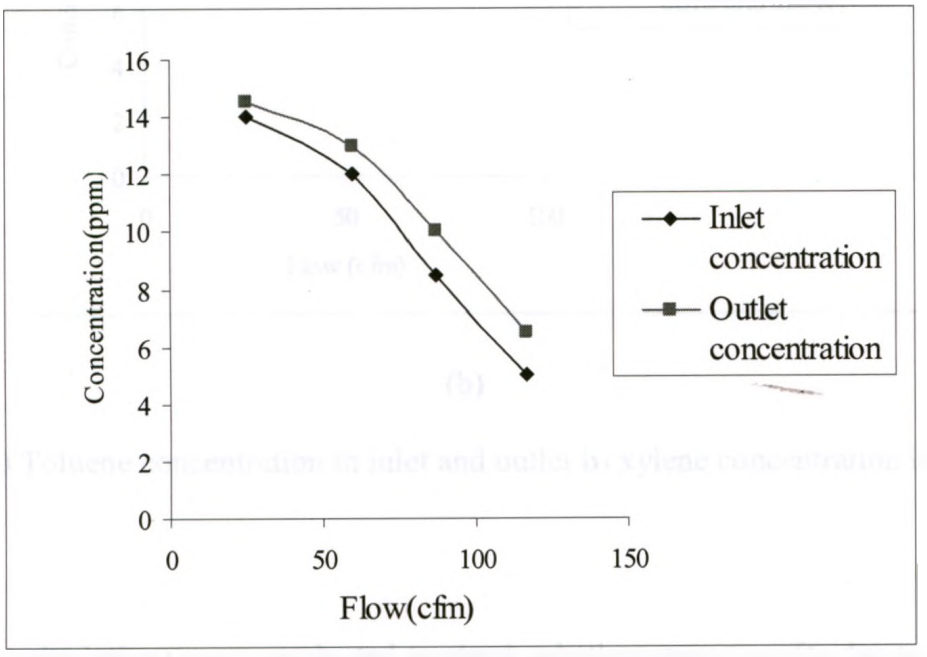
Experiments were carried out in duplicate and data were collected under steady state. The conversion of the VOCs was calculated from the difference between the inlet and outlet VOC concentrations, as:

$$\%conversion = \frac{[VOCs]_{in} - [VOCS]_{out}}{[VOCs]_{in}} \times 100$$

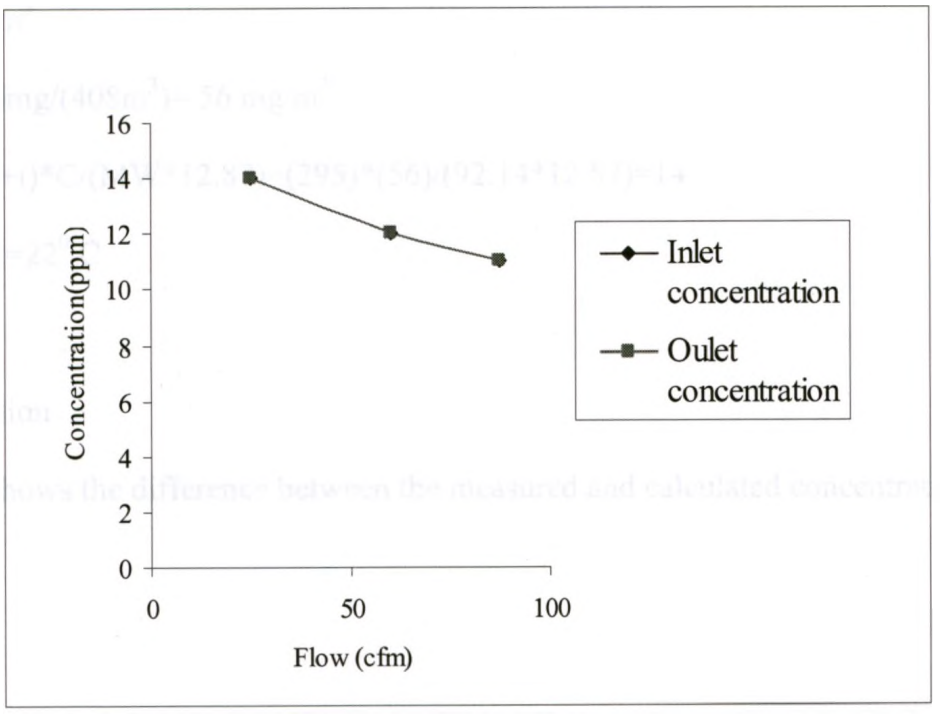
4.1 Accuracy of gas sampling system

Prior to the main experiments, accuracy of the gas sampling was carried out. This was performed by varying VOC concentration at different flow conditions. These experiments were conducted in the absence of catalysts and the light source. In case of toluene, outlet concentration was found slightly higher than inlet concentration (Fig 4.1) due to better mixing at the outlet compared to inlet. However, the difference in inlet and outlet concentrations of xylene is not that significant. Although, toluene is more volatile than xylene (vapour pressure

at 20^0 C for toluene is 2.66KPa and for xylene is1.2 Kpa.), higher amount of toulene is evaporated for the same air flow rate and needs greater mixing time. Since toluene outlet concentration in absence of light was always higher than inlet, a normalization factor was used for toluene concentration measurement at the outlet.



(a)



(b)

Figure 4.1: a) Toluene concentration in inlet and outlet **b)** xylene concentration in inlet and outlet.

Mass balance calculations were conducted to check whether mass transfer due to volatilization of known volume of VOCs and the measured concentration based on standard calibration curves were in accordance. A sample calculation using toluene is shown below:

Volumetric flow rate (Q) = 60 cfm

Volume of toluene evaporated =26.5 ml

Density of toluene=0.866 gm/ml

Mass of toluene evaporated=26.5 ml*0.866 gm/ml=23gm

Volume of air @ 4 hr = Q*t= (60*4*60) /(3.28 *3.28*3.28) =408 m^3

1ft=(1/3.28) m^3

C=(23*1000)mg/(408m^3)= 56 mg/m^3

ppmv = (273+t)*C/(MW*12.87)=(295)*(56)/(92.14*12.87)=14

Température =22^0 C

t=4 hr

C=concentration

Figure 4.2a shows the difference between the measured and calculated concentrations of toluene

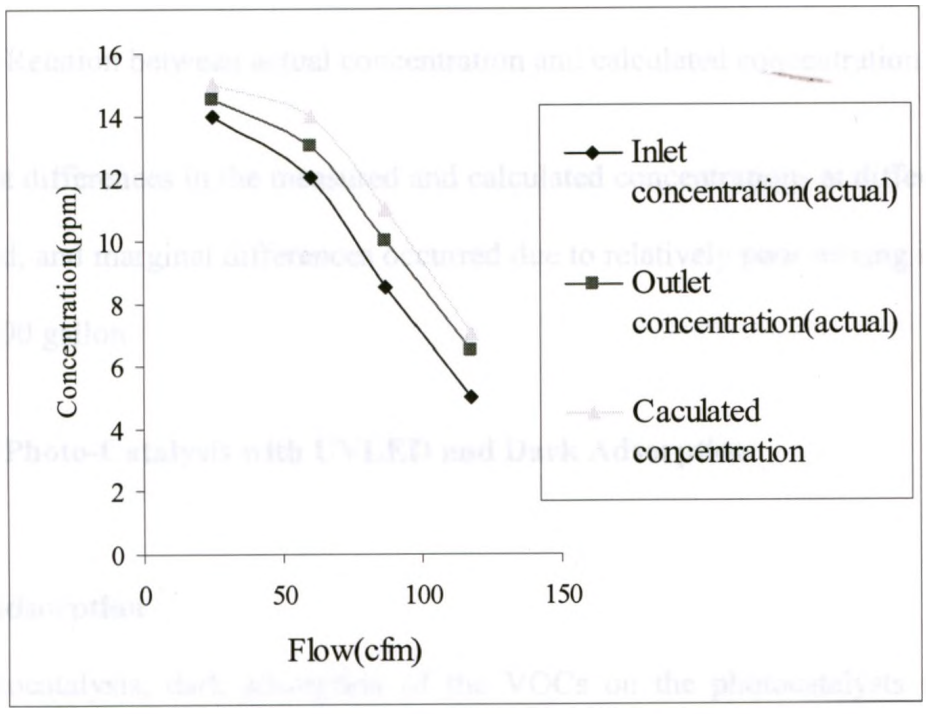


Figure 4.2a: Relation between actual concentration and calculated concentration of toluene.

Similar calculation was done for xylene and the resultant concentrations are shown in Figure 4.2.b.

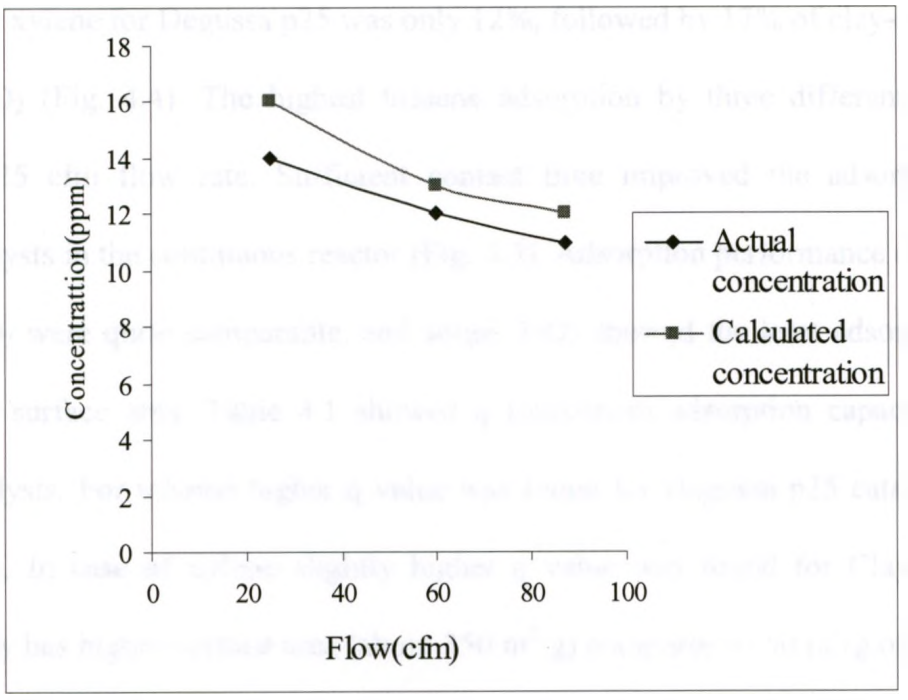


Figure 4.2b: Relation between actual concentration and calculated concentration of xylene

No significant differences in the measured and calculated concentrations at different flow rates were observed, and marginal differences occurred due to relatively poor mixing in the large air chamber of 200 gallon.

4.2 Effect of Photo-Catalysis with UVLED and Dark Adsorption

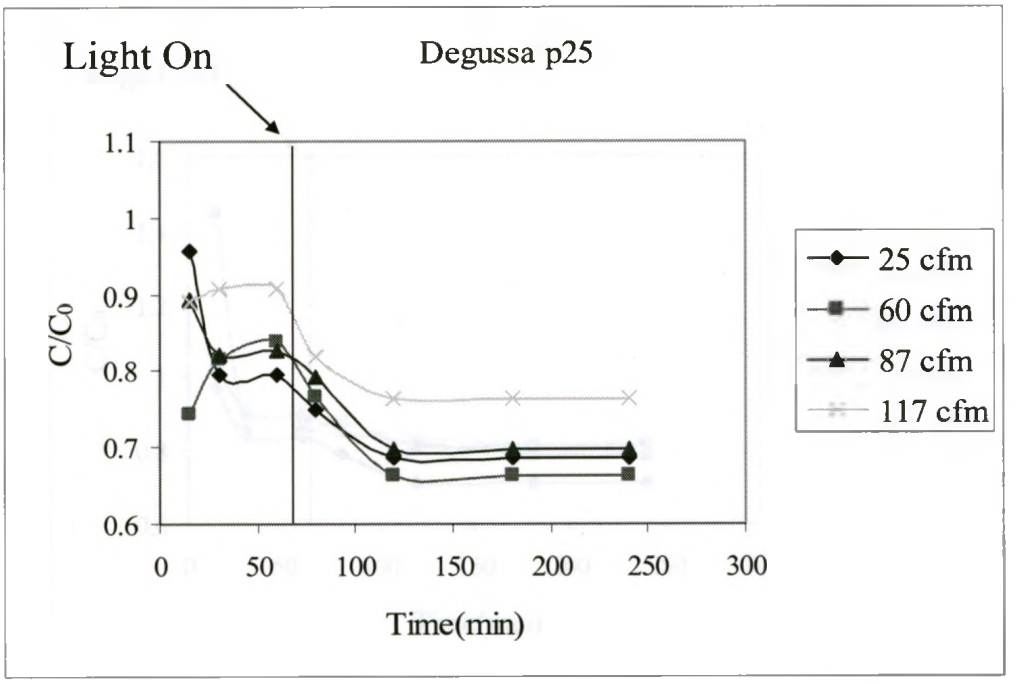
4.2.1 Dark Adsorption

Prior to photocatalysis, dark adsorption of the VOCs on the photocatalysts in absence of UVLED was established at different flow rates. Typical dark adsorption data are shown in Figure 4.3 and 4.4 for toluene and xylene, respectively. Adsorption equilibria was achieved rather fast, and the outlet concentration and C/C_0 remained fairly stable after 50-60 minutes, when the light source was turned on. The highest adsorption for toluene of 20.5% was found for Degussa p25, followed by 16.5% of clay-TiO_2, and 12% of Solgel TiO_2.(Fig. 4.3).

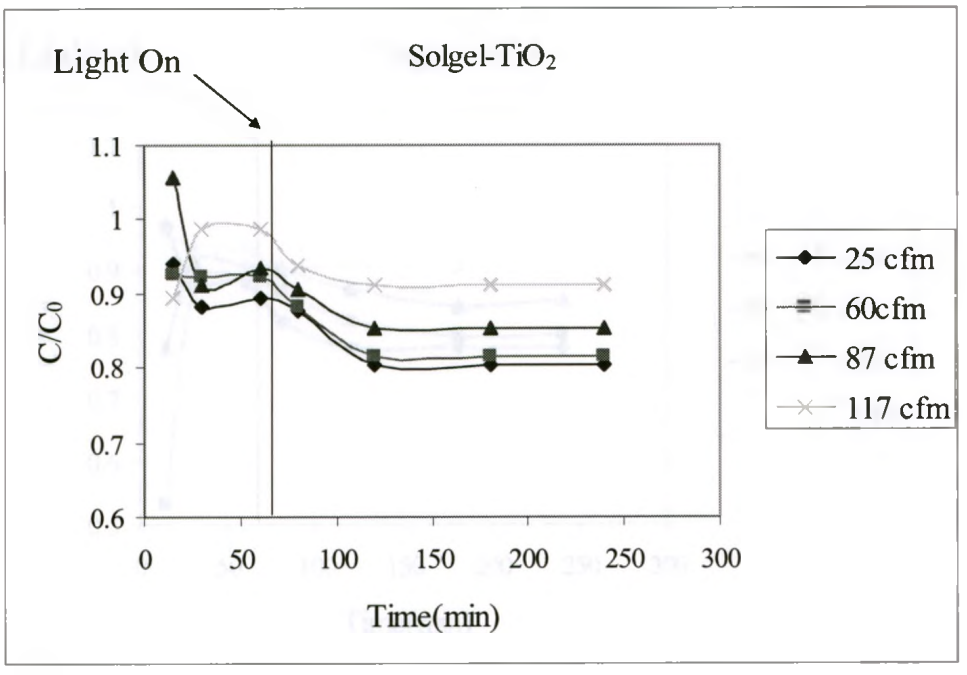
Adsorption of xylene for Degussa p25 was only 12%, followed by 17% of clay- TiO_2, and 11% of Solgel TiO_2 (Fig. 4.4). The highest toluene adsorption by three different catalysts was observed at 25 cfm flow rate. Sufficient contact time improved the adsorption on three different catalysts in the continuous reactor (Fig. 4.3). Adsorption performance of Degussa P25 and Clay TiO_2 were quite comparable, and solgel TiO_2 showed the least adsorption probably due to lower surface area. Table 4.1 showed q (maximum adsorption capacity) values for different catalysts. For toluene higher q value was found for Degussa p25 catalysts, followed by Clay-TiO_2. In case of xylene slightly higher q value was found for Clay-TiO_2 catalyst Although, clay has higher surface area (about 350 m^2/g) compared to 50 m^2/g of Degussa p25, the coating process on the mesh probably reduced the available surface area. This also explains why mixing due to higher flow rate did not cause faster adsorption probably due to most adsorption sites are due to external surface area of the catalyst.

Table 4.1: Average adsorbed VOCs (q, mg/g) on different catalysts coated mesh

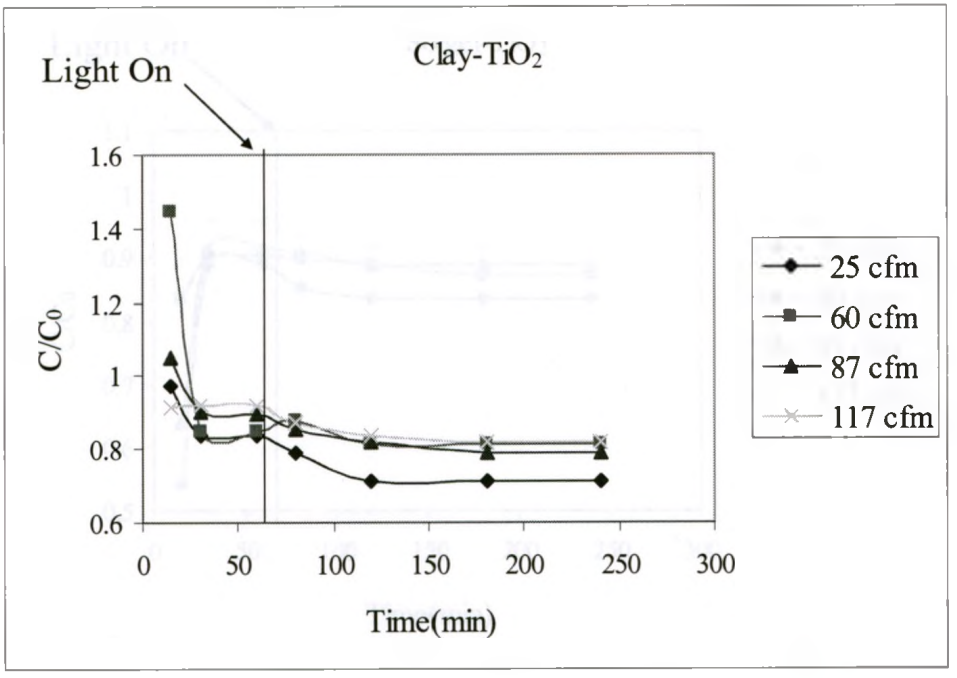
Catalysts	**Toluene**	**Xylyne**
Degussa P25	108 mg/g	79 mg/g
Clay-TiO_2	76 mg/g	88 mg/g
Solgel-TiO_2	35 mg/g	51 mg/g


Light On
Degussa p25
1.1
1
0.9
0.8
0.7
0.6
C/C0
0
50
100
150
200
250
300
Time(min)
25 cfm
60 cfm
87 cfm
117 cfm

(a)

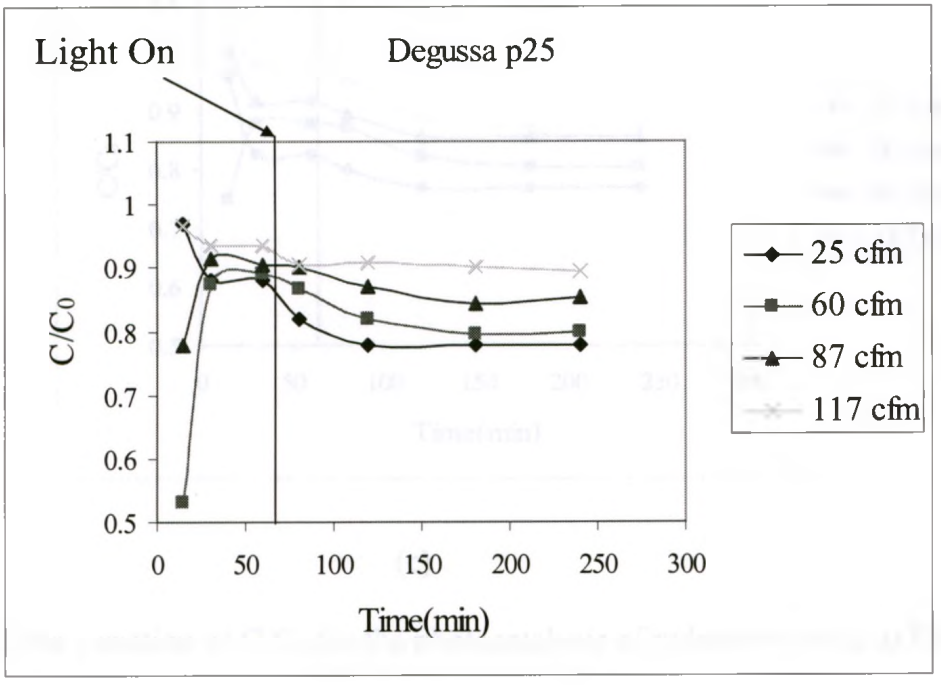

Light On
Solgel-TiO2
1.1
1
0.9
0.8
0.7
0.6
C/C0
0
50
100
150
200
250
300
Time(min)
25 cfm
60cfm
87 cfm
117 cfm

(b)

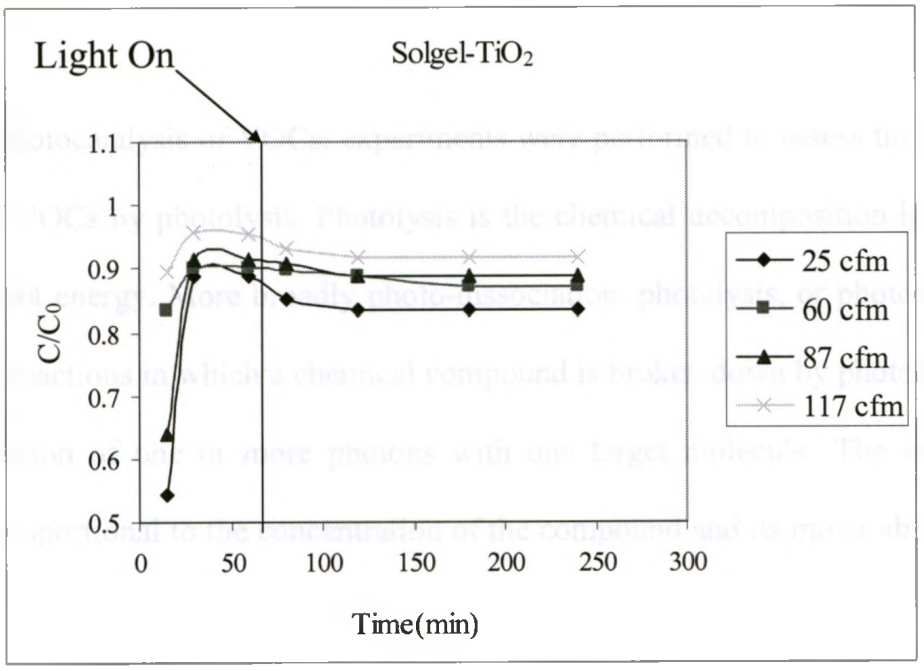


(c)

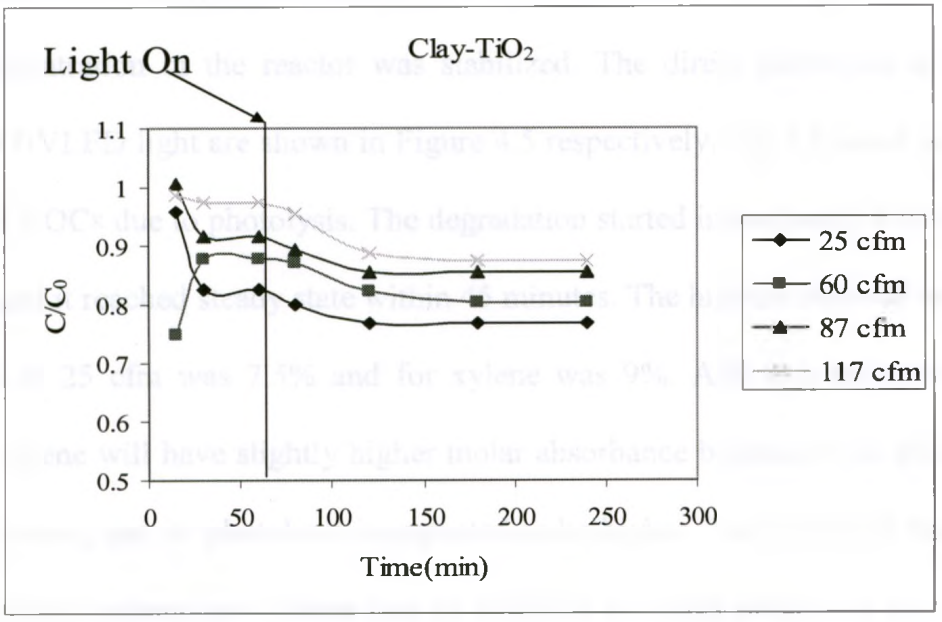
Figure 4.3: C/C_0 for the photocatalysis of toluene by using a) Degussa p25 b) Solgel-TiO_2 c) Clay TiO_2.



(a)



(b)



(c)

Fig 4.4: Time variation of C/C_0 for the photocatalysis of xylene by using a) Degussa p25 b) Solgel-TiO_2 c) Clay TiO_2.

4.2.2 Photolysis

Prior to the photocatalysis of VOCs, experiments were performed to assess the decomposition efficiency of VOCs by photolysis. Photolysis is the chemical decomposition induced by light or other radiant energy. More broadly photo-dissociation, photolysis, or photo-decomposition are chemical reactions in which a chemical compound is broken down by photons. It is defined as the interaction of one or more photons with one target molecule. The amount of light absorbed is proportional to the concentration of the compound and its molar absorbance at that wavelength.

Photolysis tests were carried out by passing the same concentration of VOCs through the reactor in absence of catalysts but with UVLED light turned on. The light was switched on once the concentration in the reactor was stabilized. The direct photolysis of toluene and xylene by 60 UVLED light are shown in Figure 4.5 respectively. Fig 4.5 a and 4.5 b show the % removal of VOCs due to photolysis. The degradation started immediately after the light was switched on and it reached steady state within 45 minutes. The highest removal for toluene due to photolysis at 25 cfm was 7.5% and for xylene was 9%. Although not measured in the experiment, xylene will have slightly higher molar absorbance because of its higher molecuar weight than tolune, and its photolysis is expected to be higher. The results of this experiment also point out that toluene and xylene can be oxidized by direct photolysis using very small power of UVLED. The effect of flow rate also has similar effect as was seen earlier, that is, the degradation increased with decreasing flow rate due to increase in residence time.

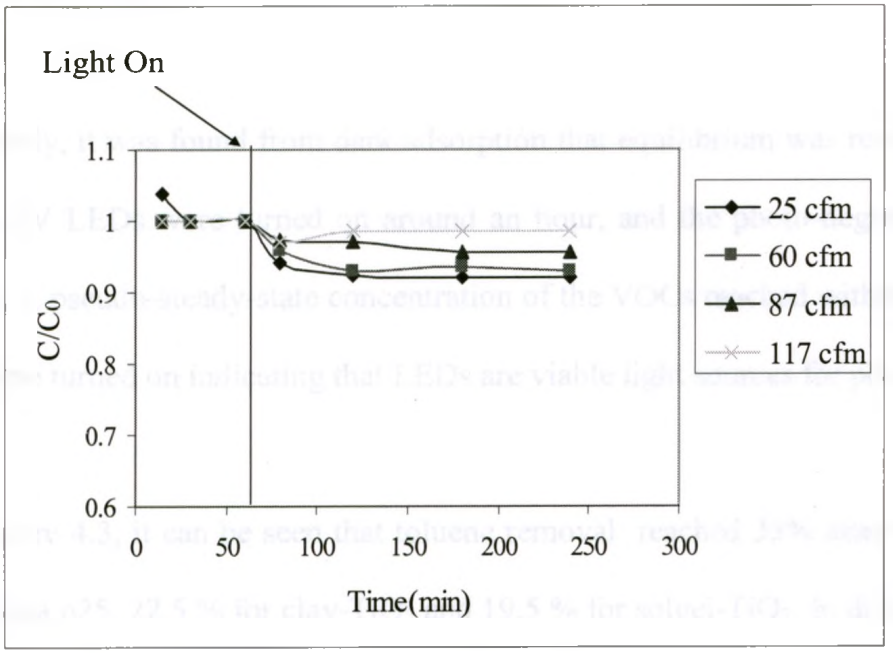


Fig 4.5a: Time variation of C/C_0 for the photolysis of toluene

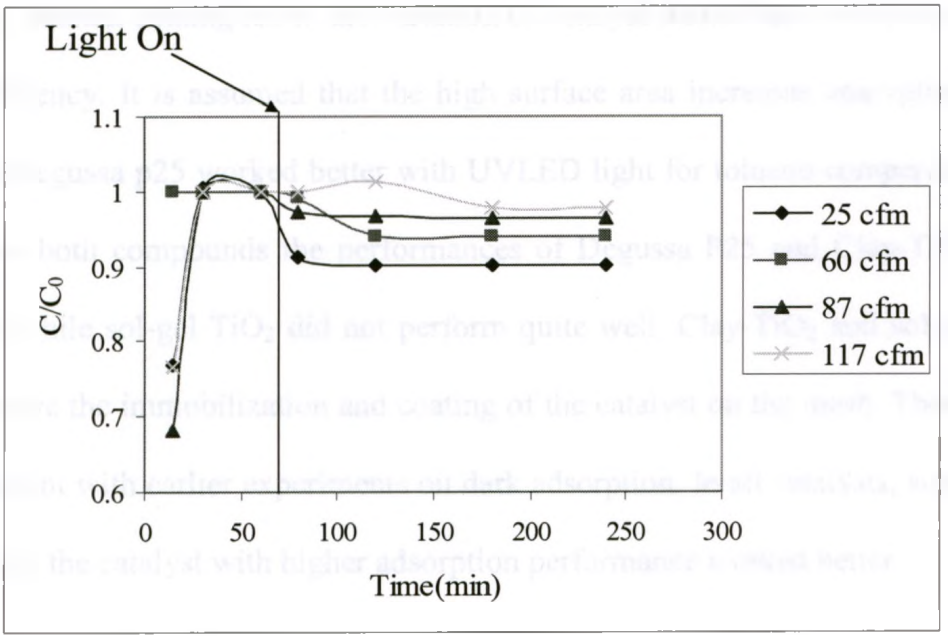


Figure 4.5b: Time variation of C/C_0 for the photolysis of xylene

4.2.3 Photocatalysis

In this study, it was found from dark adsorption that equilibrium was reached after 30 minutes and the UV LEDs were turned on around an hour, and the photo-degradation of VOCs was initiated. A pseudo-steady-state concentration of the VOCs reached within 30 minutes after the LEDs were turned on indicating that LEDs are viable light sources for photo-catalysis.

From Figure 4.3, it can be seen that toluene removal reached 33% after 60 min of irradiation for Degussa p25, 22.5 % for clay-TiO_2 and 19.5 % for solgel-TiO_2. In this experiment, the flow was kept constant at 25 cfm. In case of xylene removal, it reached 23% for clay-TiO_2, 22.5 % for Degussa p25 and 16.5% for solgel TiO_2 at 25 cfm (Fig 4.4).

In this study, manual coating led to the variation of catalyst surface area which might affect the removal efficiency. It is assumed that the high surface area increases adsorption site. It was noticed that Degussa p25 worked better with UVLED light for toluene compared to other two catalysts. For both compounds the performances of Degussa P25 and Clay-TiO_2 were quite comparable, while sol-gel TiO_2 did not perform quite well. Clay-TiO_2 and sol-gel TiO_2 were used to improve the immobilization and coating of the catalyst on the mesh. These results also are in agreement with earlier experiments on dark adsorption. In all catalysts, since TiO_2 is the active catalyst, the catalyst with higher adsorption performance worked better.

4.3 Effect of Flow

In this study, four different flows were used that were 25 cfm, 60 cfm, 87 cfm and 117 cfm. The influence of flow rate on the degradation of VOCs was illustrated in the following figure. Flow rate is a crucial factor for the PCO of VOCs. The flow rate affects the photo-catalytic reaction by changing the convective mass transfer and residence time in the reactor. Increased flow rate thus has two counteracting effects of improved mass transfer and lower residence time on the photo-catalytic reaction. The increased flow rate improves the photocatalytic reaction by increasing diffusion between VOCs (Yu et al., 2007). It seems in our experiments, that the effect of the reduction of the residence time is more predominant than the improvement of mass transfer by diffusion. The immobilized catalysts on mesh have mostly external surface area, thus diffusion of the VOCs into the pores is not an issue.

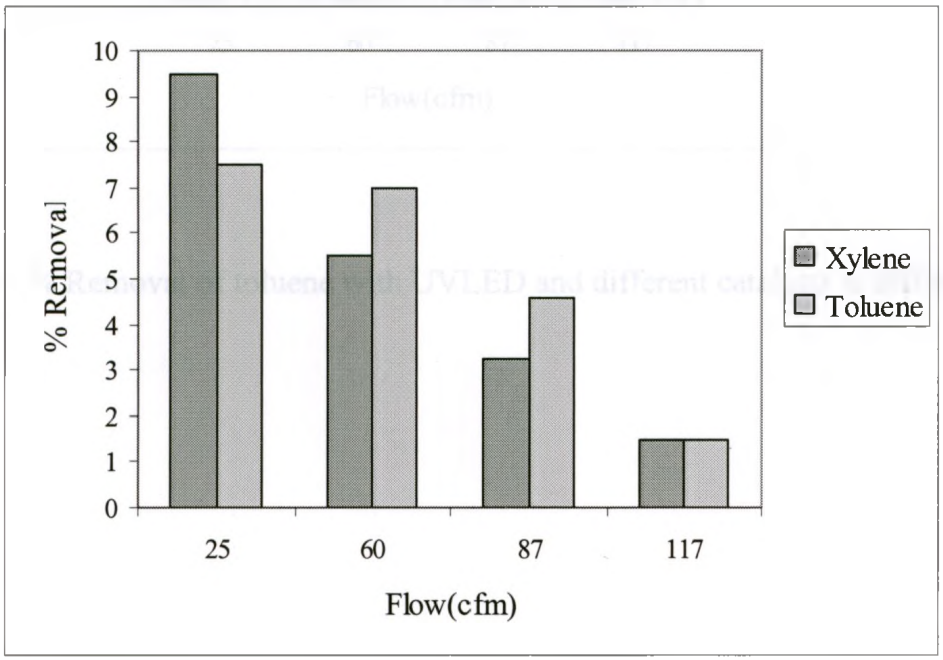


Figure 4.6: VOCs removal with UVLED photolysis at different flow conditions.

Figure 4.6 shows the effect of flow rate on degradation of the VOCs by the use of UVLED light. Between toluene and xylene at 25 cfm, % removal of xylene was (9.5%) higher than toluene (7.5%). At 117 cfm removal of VOCs was same, which was only1.5%. The similar effect of flow rate on photocatalysis of the VOCs can be seen in Figure 4.7a However for all flow conditions toluene removal was higher than xylene due to its better adsorption.

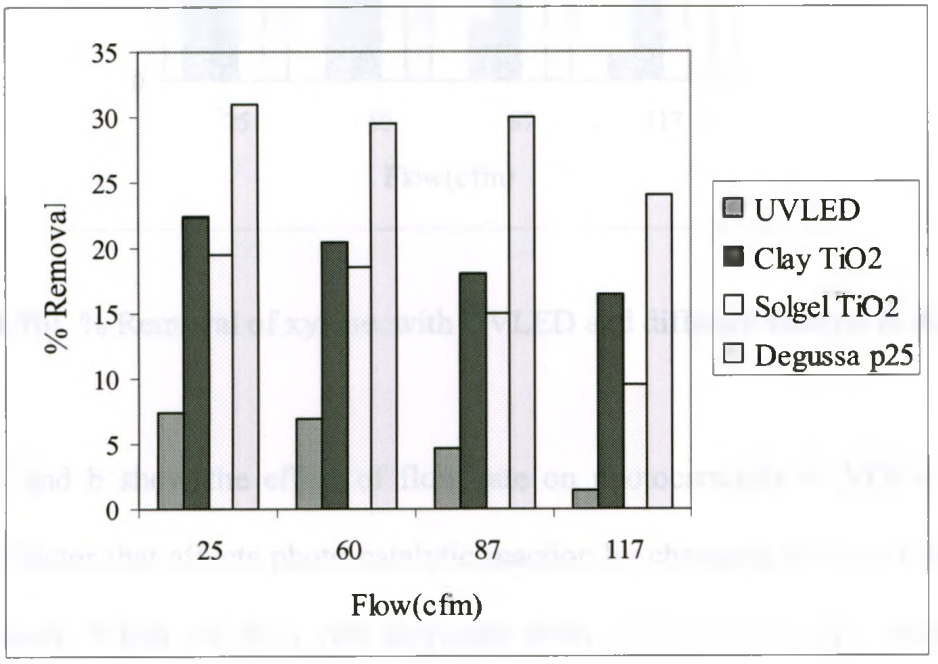


Fig 4.7a: % Removal of toluene with UVLED and different catalysts at different flows.

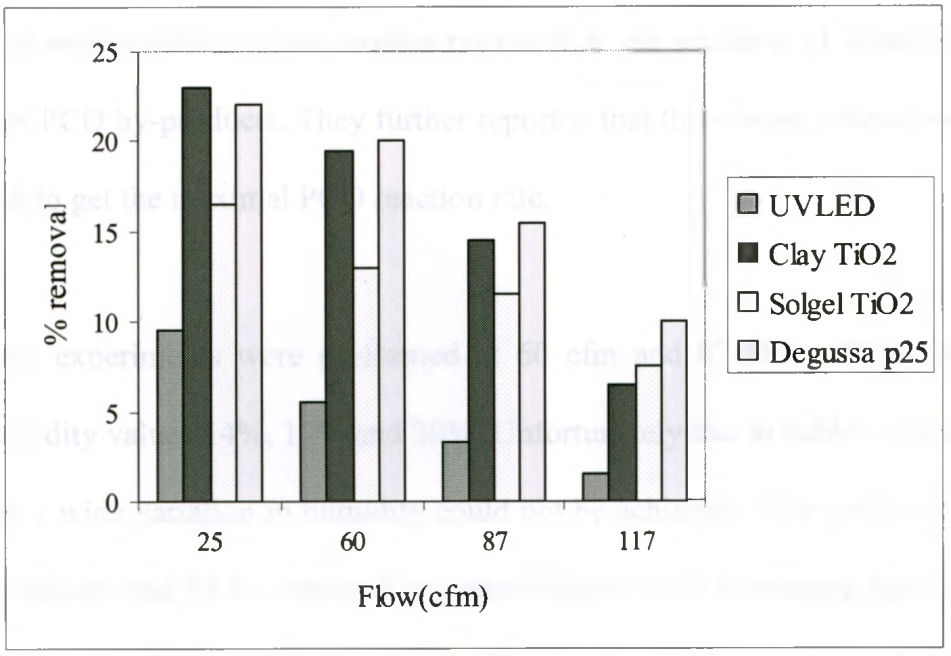


Fig 4.7b: % Removal of xylene with UVLED and different catalyst at different flows

Fig 4.7 a and b show the effect of flow rate on photocatalysis of VOCs. Flow rate is an important factor that affects photo-catalytic reaction by changing the convective mass transfer and diffusion. When the flow rate increases from 25 cfm to117 cfm degradation removal decreased from 33% to 9.5% for toluene and for xylene 23% to 7.5%.

4.4 Effect of humidity

Relative humidity represents one of the most important parameters for PCO in the gas phase. According to Vildozo et.al. (2010), the impact of humidity has a great effect on the efficiency in the air treatment. In the absence of water vapour, the PCO of some VOCs were seriously retarded. On the other hand, with high percentages of water vapour on the catalyst surface

there is an inhibition in reaction rate because of the effect of competitive adsorption between water vapour and pollutant. Some studies proved that the presence of water also affects the generation of PCO by-products. They further reported that there is an optimal concentration of water vapour to get the maximal PCO reaction rate.

In this study, experiments were performed at 60 cfm and 87 cfm flow rate using three different humidity values 14%, 17% and 20%. Unfortunately due to bubbler system used in the experiments, a wide variation in humidity could not be achieved. The results shown in Figure 4.8 a and b indicate that VOCs removal increased slightly with increasing humidity. However, due to lower range of humidity and small differences in percent removal, the quantitative accuracy of data can not be ascertained.

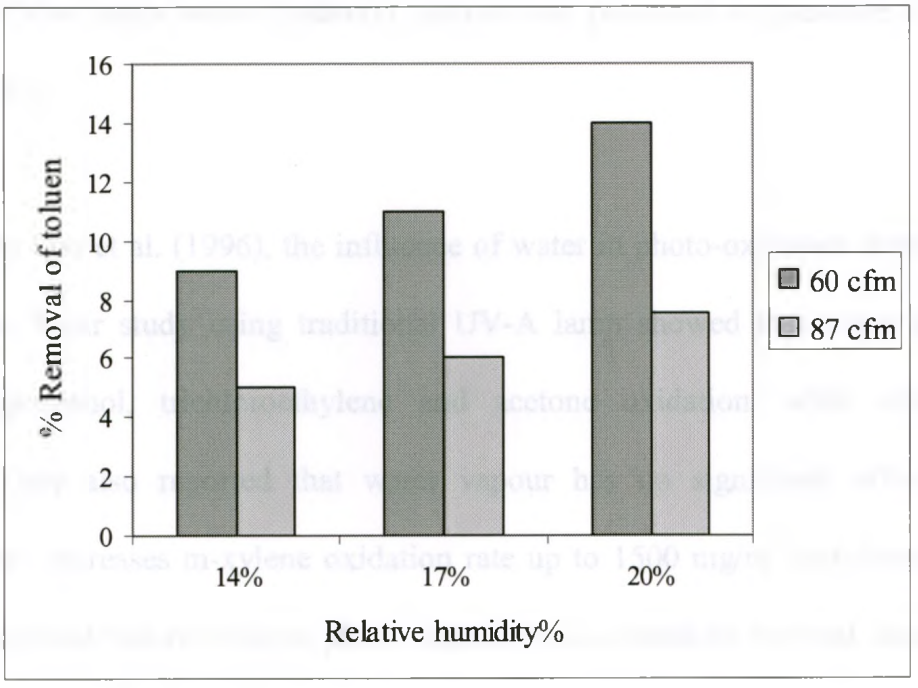


Figure 4.8a: % Removal of toluene with %Relative Humidity (RH) using Sol-gel-TiO_2

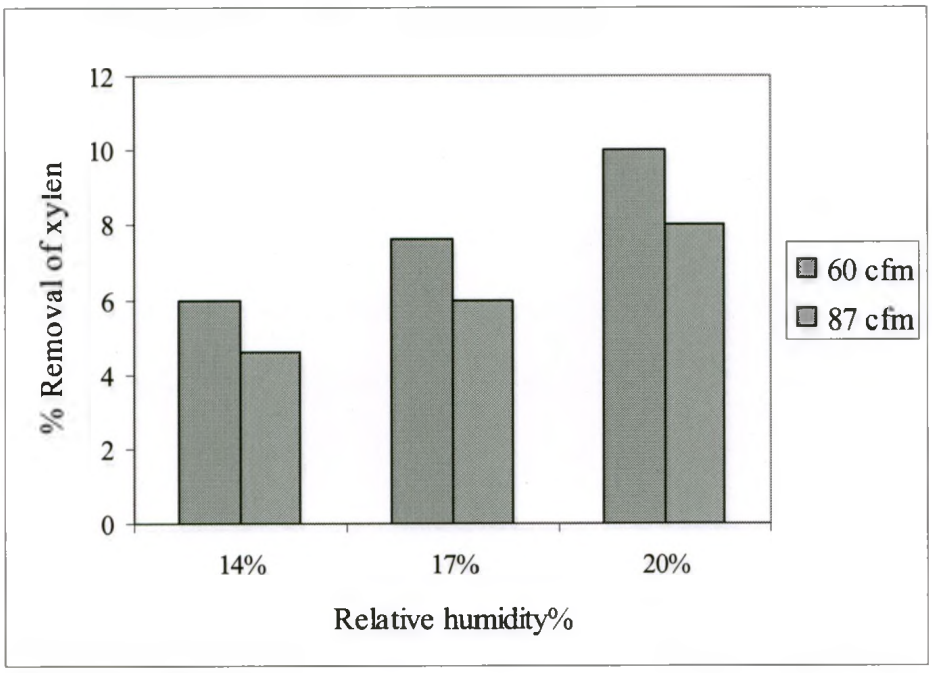


Figure 4.8b: % Removal xylene with %Relative Humidity (RH) using Solgel-TiO_2

These results indicate that the mechanism of photocatalysis using UVLED is similar to using traditional UV-A lamp where hydroxyl radicals are produced in presence of humidity and irradiated TiO_2.

According to Luo et al. (1996), the influence of water in photo-oxidation depends also on the contaminant. Their study using traditional UV-A lamp showed that water vapour strongly inhibits isopropanol, trichloroethylene and acetone oxidation, while enhances toluene oxidation. They also reported that water vapour has no significant effect on 1-butanol oxidation but increases m-xylene oxidation rate up to 1500 mg/m^3 and decreases thereafter. They also reported that no toluene photo-degradation occurred in the total absence of water in the toluene–air mixture. Toluene oxidation rate was enhanced by water concentrations at about 23–40% relative humidity and was somewhat inhibited at 60% RH (Luo et al., 1996).

Obee (1995) reported that the degradation rate increased by an increase in concentration of $OH^{\cdot}$ radicals, which were supposed to be the primary oxidant during PCO (Obee, 1995). The water molecule adsorbed on the surface of the photo-catalyst would be oxidized to hydroxyl radical by the hole generated by photon absotpion of the catalyst as described in Chapter 2. Increase of relative humidity add to the concentration of hydroxyl radical which is the major free radical attacking and decomposing VOC molecule (Yu et al. 1996).

4.5 Effect of light intensity

In this work, two sets of UV LEDs of 360 nm were used. In one set, 60 LEDs with output power of 1200 μW for LED were used. In another set, 120 LEDs of similar output power were used. The intensity for 60 LED was 0.077mw/cm^2 and 120 light was 0.155mw/cm^2.

The effect of light intensity has been investigated for the flow rates of 60 cfm and 87 cfm. Figure 4.9 a and 5b show the percent removal of VOCs with number of light at different flows. When number of light increased from 60 to 120, output power was increased by double which increased the removal rate. These experiments were conducted in absence of any catalysts, and only the effect of photolysis was investigated.

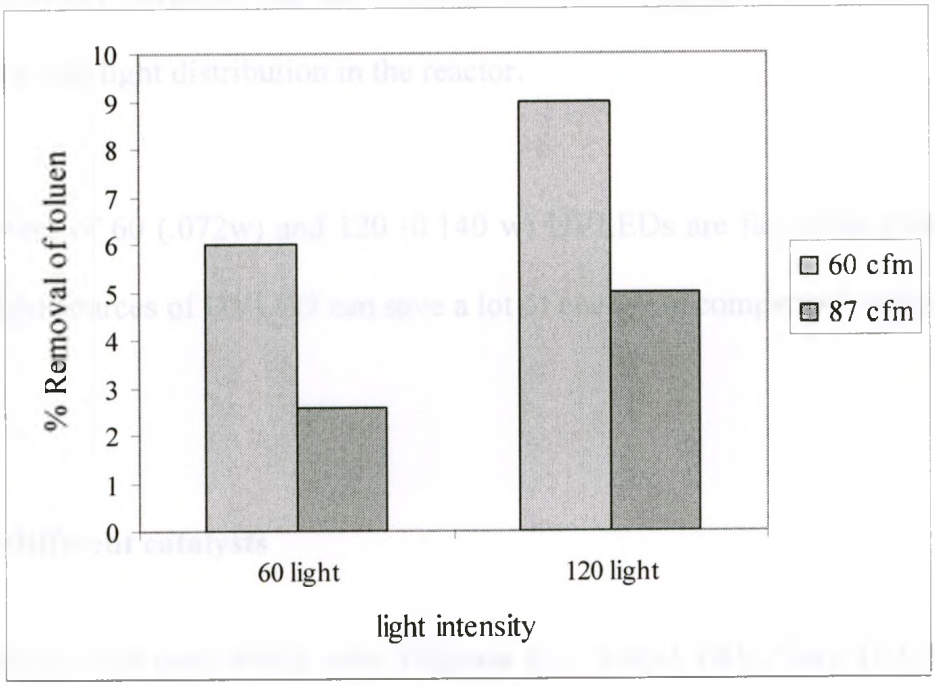


Figure 4.9.a: % Removal of toluene with number of light at different flow conditions

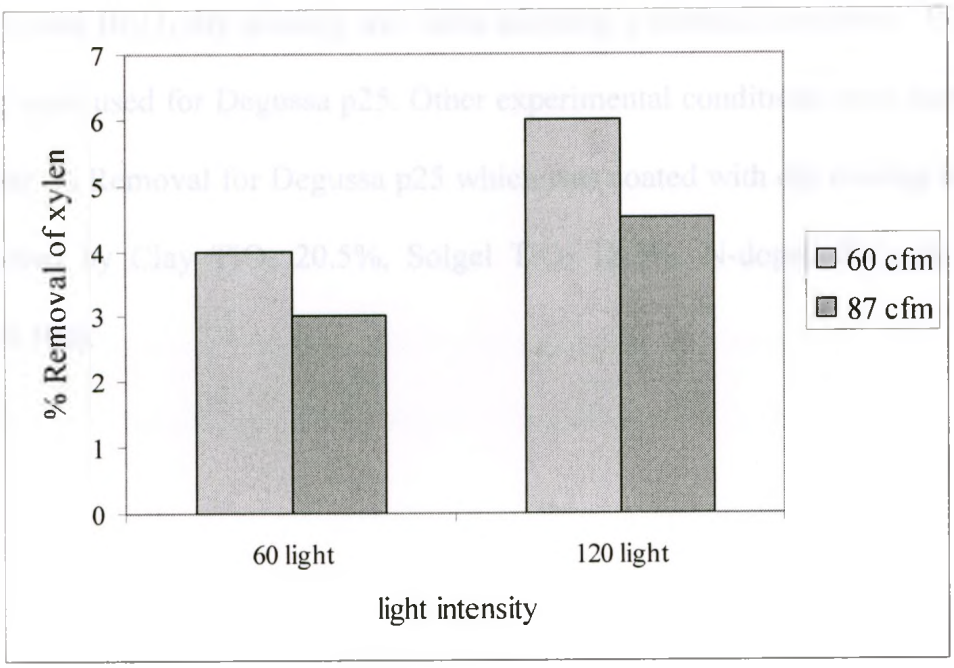


Figure 4.9.b % Removal of xylene with number of light at different flow conditions

However, the effect removal was not doubled due to doubling of the intensity, indicating inefficient flow and light distribution in the reactor.

The total powers of 60 (.072w) and 120 (0.140 w) UVLEDs are far lower than those of UV lamps. The light sources of UVLED can save a lot of energy in comparison with the traditional UV lamps.

4.6 Effect of different catalysts

Different catalyst were used which were Degussa p25, Solgel TiO_2, Clay-TiO_2,N-doped TiO_2 and Bi_2O_3. N-doped TiO_2 and Bi_2O_3 catalysts were obatined from Vive-Nano, a collaboarting comapny in this project. Manual coating was used for Solgel TiO_2 and Clay-TiO_2. For N-doped TiO_2 and Bi_2O_3 dip coating was done adopting a method developed. Both manual and dipcoating were used for Degussa p25. Other experimental conditions were kept similar for all the catalysts. % Removal for Degussa p25 which was coated with dip coating the removal was 32% followed by Clay TiO_2 20.5%, Solgel TiO_2 18.5%, N-doped TiO_2 20.5% and Bi_2O_3 28%.(Fig 4.10a).

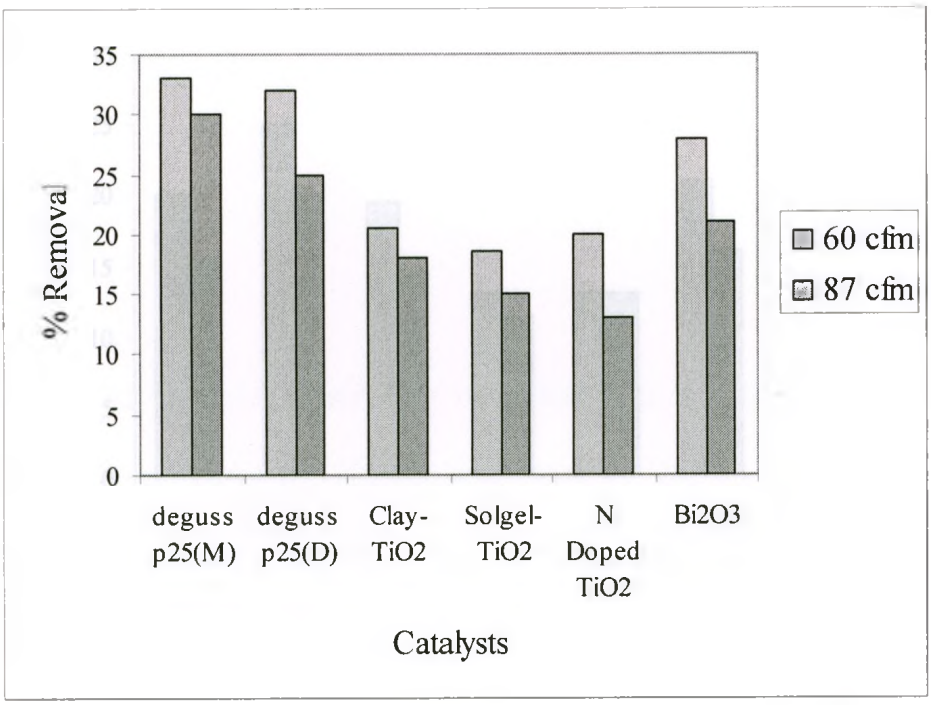


Figure 4.10a: % Removal of toluene with different catalysts

In this experiment for xylene, highest removal was found for Degussa 25 which was 25% using dip coating at 60 cfm. Other conditions of the experiment kept same for every catalysts. % Removal for Degussa p25 which was coated manually, he removal was 20% followed by Clay TiO_2 19.5%, Solgel TiO_2 13% Ndoped TiO_2 13% and Bi_2O_3 21%.(Fig 4.10b).

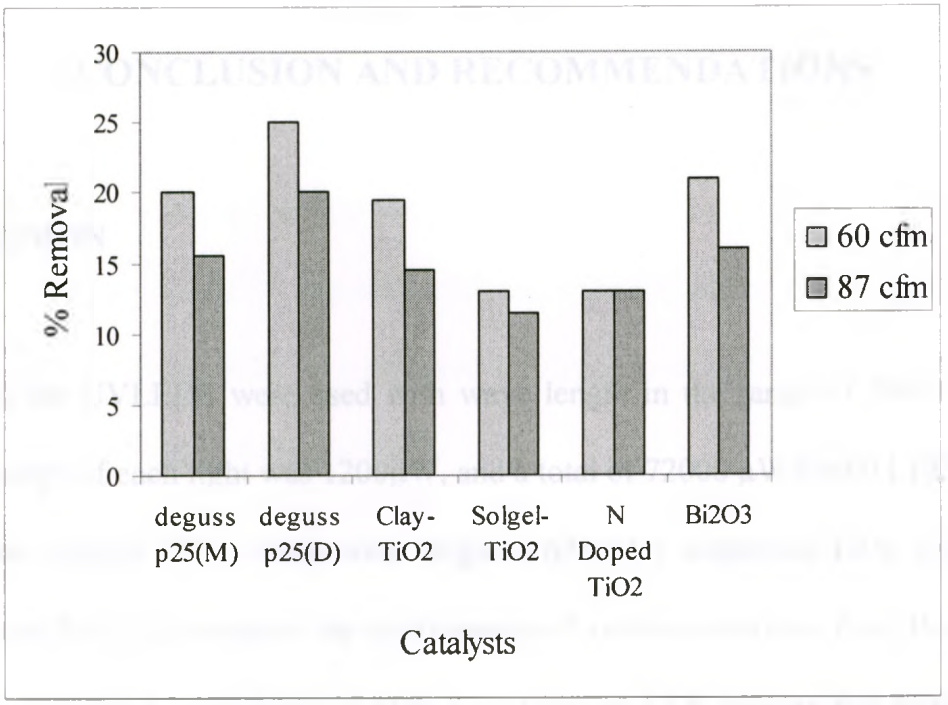


Figure 4.10b: % Removal of xylene with different catalysts

It showed from the results that the coating, which was done manually gave better result for toluene due to higher loading of catalyst. In contrays, by dip coating only three layers of catalyst were coated although the coating was uniform. Further studies are required for optimum coating of catalysts, which could not be completed due to lack of time.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

In this study, the UVLEDS were used with wave length in the range of 360-363 nm wave length and energy of each light was 1200μW, and a total of 72000 μW for 60 LEDS. 5 types of catalysts were used for PCE, which were Degussa p25, clay supported TiO_2, solgel-TiO_2, N-doped TiO_2 and Bi_2O_3 to compare the performance of various catalysts. Four flow rates were used: 25 cfm, 60 cfm, 87 cfm and 117 cfm. Two types of VOC compounds were used which were toluene and xylene. An indoor air purification device was set up at a pilot scale., which consisted of a reactor and a buffer tank. Buffer tank was installed to obtain a stable flow of indoor air.

Manual and dip-coating methods were used to immobilize the catalysts. For Clay-TiO_2 and Solgel TiO_2 manual coating was used. For N-doped TiO_2 and Bi_2O_3, dip coating was used. However, for Degussa p25 both manual and dip coating were used.

The results showed the effect of different parameters (catalyst, humidity, intensity, flow rate and types of coating) for the removal of VOCs from air. Under similar condition, the photo oxidation rate of toluene was greater than xylene, and the highest removal was obtained for 25 cfm flow. Photolysis using UVLED alone can remove VOCs and only 7.5% toluene, and 9% xylene were removed.

The highest adsorption of toluene was found to be 20.5% using Degussa p25 and 60 LED. In case of xylene, the highest removal was 17% using clay-TiO_2 catalyst. Both Degussa P25 and Clay TiO_2 showed comparable performance. The results showed the effect of relative humidity on VOC removal from indoor air was marginal in the small range of humidity. The results indicated that increasing LED intensity and moisture increases VOC removal and the mechanism of removal is similar to traditional UV light sources. Therefore, UVLED can be effectively used as radiation source for PCO.

5.2 RECOMMENDATIONS FOR FUTURE WORK

Photo-catalytic process using UVLED is a new concept. Long term comprehensive studies are required for large scale application.

The following are recommended for future studies.

1) Expand studies to other VOCs or pollutants of concern.

2) Perform PCO studies on systems that involve mixtures of contaminants that are more representative of typical indoor air environments.

3) Develop optimum operating parameters to get better designs and performance.

4) Perform economic studies to determine the cost of the system.

5) Establish operational life of the system with UVLED.

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APPENDEX

Table: Concentration and % removal of toluene by photolysis at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	13.8	13.8	0	1
30	13.8	13.8	0	1
60	13.8	13.8	0	1
80	13.8	13	5	0.94203
120	13.8	12.7	8	0.92029
180	13.8	12.7	8	0.92029
240	13.8	12.7	8	0.92029

Table: Concentration and % removal of toluene by photolysis at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	15.38	15.38	0	1.07542
30	13.8	13.8	0	1
60	13.8	13.8	0	1
80	13.8	13	5	0.94203
120	13.8	12.8	7	0.92754
180	13.8	12.7	7	0.92029
240	13.8	12.7	7	0.92029

Table: Concentration and % removal of toluene by photolysis at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	8.5	8.5	0	1
30	8.5	8.5	0	1
60	8.7	8.5	0	1
80	8.7	8.4	3	0.96551
120	8.7	8	8	0.91954
180	8.7	8.1	6	0.93103
240	8.7	8	8	0.91954

Table: Concentration and % removal of toluene by photolysis at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	9.07	9.07	0	1
30	9.07	9.07	0	1
60	9.07	9.07	0	1
80	9.07	8.65	5	0.95369
120	9.07	8.54	6	0.94157
180	9.07	8.54	6	0.94157
240	9.07	8.54	6	0.94157

Table: Concentration and % removal of toluene by photolysis at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	8.7	8.2	0	1
30	7.5	7.5	0	1
60	7.5	7.5	0	1
80	7.5	7.2	4	0.96
120	7.5	7.1	6.5	0.93915
180	75	7.1	6.5	0.93915
240	7.5	7.1	6.5	0.93915

Table: Concentration and % removal of toluene by photolysis at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	8.54	8.54	0	1
30	8.54	7.75	0	1
60	7.48	7.48	0	1
80	7.48	7.38	1	0.98663
120	7.48	7.48	0	1
180	7.48	7.28	2.6	0.97326
240	7.48	7.28	2.6	0.97326

Table: Concentration and % removal of toluene by photolysis at 117 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	8	8.2	0	1
30	6.2	6.7	0	1
60	6.2	6.7	0	1
80	6.5	6.1	2	0.93846
120	6.2	6	3	0.96774
180	6.2	6	3	0.96774
240	6.2	6	3	0.96774

Table: Concentration and % removal of toluene by photolysis at117 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	6.28	3.28	0	1
30	4.32	4.32	0	1
60	4.32	4.32	0	1
80	4.32	4.32	0	1
120	4.32	4.32	0	1
180	4.32	4.32	0	1
240	432	4.32	0	1

Table: Concentration and % removal of toluene by photo catalysis using Solgel TiO_2 at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	13	9	30	0.69231
30	13	11.7	10	0.9
60	13	11.6	10	0.89231
80	13	11	15	0.84615
120	13	10.1	22	0.77692
180	13	10.1	22	0.77692
240	13	10.1	22	0.77692

Table : Concentration and % removal of toluene by photo catalysis using Solgel TiO_2 at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	11.17	13.28	0	1.1889
30	14.33	12.39	14	0.86462
60	13.81	12.39	10	0.89718
80	13.81	12.5	9	0.90514
120	13.81	11.43	17	0.82766
180	13.81	11.43	17	0.82766
240	13.81	11.43	17	0.82766

Table: Concentration and % removal of toluene by photo catalysis using Solgel TiO_2 at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	13	13	0	1
30	11	10	9	0.90909
60	11	10	9	0.90909
80	11	9.5	14	0.86364
120	11	8.9	19	0.80909
180	11	8.9	19	0.80909
240	11	8.9	19	0.80909

Table: Concentration and % removal of toluene by photo catalysis using Solgel TiO_2 at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	6.96	5.91	15	0.84914
30	12.22	11.43	6	0.93535
60	12.22	11.43	6	0.93535
80	12.22	11	10	0.9
120	12.22	10.06	18	0.82324
180	12.22	10.06	18	0.82324
240	12.22	10.06	18	0.82324

Table: Concentration and % removal of toluene by photo catalysis using Solgel TiO_2 at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	3.5	4	0	1.14286
30	7.5	6.9	7	0.92
60	7.5	6.9	7	0.92
80	7.5	6.8	9	0.90667
120	7.5	6.4	15	0.85333
180	7.5	6.4	15	0.85333
240	7.5	6.4	15	0.85333

Table: Concentration and % removal of toluene by photo catalysis using Solgel TiO_2 at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	7.5	7.28	3	0.97067
30	10.64	9.59	9	0.90132
60	10.12	9.59	5	0.94763
80	10.12	9.44	7	
120	10.12	8.64	15	0.85375
180	10.12	8.64	15	0.85375
240	10.12	8.64	15	0.85375

Table : Concentration and % removal of toluene by photo catalysis using Solgel TiO_2 at 117 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	7	7	0	1
30	4	3.9	2	0.975
60	4	3.9	2	0.975
80	4	3.8	5	0.95
120	4	3.6	10	0.9
180	4	3.6	10	0.9
240	4	3.6	10	0.9

Table: Concentration and % removal of toluene by photo catalysis using Solgel TiO_2 at 117 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	2.49	1.96	0	0.78715
30	4.86	4.86	0	1
60	4.86	4.86	0	1
80	4.86	4.5	7	0.92593
120	4.86	4.48	7	0.92181
180	4.86	4.48	7	0.92181
240	4.86	4.48	7	0.92181

Table: Concentration and % removal of toluene by photo catalysis using Clay -TiO_2 at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	14	14	0	1
30	14.3	12.2	15	0.85315
60	14.3	12.2	15	0.85315
80	14.3	11.01	23	0.76993
120	14.3	11.01	23	0.63636
180	14.3	11.01	23	0.63636
240	14.3	11.01	23	0.63636

Table: Concentration and % removal of toluene by photo catalysis using Clay -TiO_2 at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	8.5	8	5	0.941176
30	14.3	11.7	18	0.818181
60	14.3	11.7	18	0.818181
80	14.3	11.5	20	0.80419
120	14.3	11.2	22	0.783216
180	14.3	11.2	22	0.783216
240	14.3	11.2	22	0.783216

Table: Concentration and % removal of toluene by photo catalysis using Clay -TiO_2 at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	2	3.9	0	1.95
30	3.9	3.3	12	0.84615
60	3.9	3.3	12	0.84615
80	3.9	3.6	8	0.92308
120	3.9	3.2	18	0.82051
180	3.9	3.2	21	0.82051
240	3.9	3.2	21	0.82051

Table: Concentration and % removal of toluene by photo catalysis using Clay- TiO_2 at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	11.2	10.6	5	0.94642
30	12	10.28	14	0.85666
60	12	10.28	14	0.85666
80	12	10	17	0.83333
120	12	9.6	20	0.8
180	12	9.6	20	0.8
240	12	9.6	20	0.8

Table: Concentration and % removal of toluene by photo catalysis using Clay- TiO_2 at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	8	9		1.1465
30	7.9	7.1	10	0.90446
60	7.8	7	10	0.89172
80	7.8	6.5	17	0.83333
120	7.8	6.3	19	0.80255
180	7.9	6.3	19	0.80255
240	7.9	6.3	19	0.80255

Table: Concentration and % removal of toluene by photo catalysis using Clay- TiO_2 at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	10.6	10.12	5	0.95471
30	10.5	9.45	10	0.9
60	10.5	9.45	10	0.9
80	10.5	9.15	13	0.87142
120	10.5	8.715	17	0.83
180	10.5	8.175	17	0.77857
240	10.5	8.175	17	0.77857

Table: Concentration and % removal of toluene by photo catalysis using Clay- TiO_2 at 117 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	3.5	3.4	2.85	0.94444
30	3.6	3.3	8	0.91666
60	3.6	3.3	8	0.91666
80	3.6	3.1	14	0.86111
120	3.6	3	17	0.83333
180	3.5	2.9	17	0.80555
240	3.5	2.9	17	0.80555

Table: Concentration and % removal of toluene by photo catalysis using Clay -TiO_2 at 117 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	4.3	3.8	11	0.88372
30	5.38	4.96	8	0.92193
60	5.38	4.96	8	0.92193
80	5.38	4.77	11	0.88662
120	5.38	4.49	16	0.83457
180	5.38	4.49	16	0.83457
240	5.38	4.49	16	0.83457

Table: Concentration and % removal of toluene by photo catalysis using Degussa p25 at 25 cfm

Time	Inlet(ppm)	Outlet(ppm)	% Removal	C/Co
15	14.9	14.9	0	1
30	14.9	12.2	18	0.81879
60	14.9	12.2	18	0.81879
80	14.9	11.5	23	0.77181
120	14.9	10.6	28	0.71141
180	14.9	10.6	28	0.71141
240	14.9	10.6	28	0.71141

Table: Concentration and % removal of toluene by photo catalysis using Degussa p25 at 25 cfm

Time	Inlet(ppm)	Outlet(ppm)	% Removal	C/Co
15	13.3	12.1	9	0.90977
30	13.8	10.64	23	0.77101
60	13.8	10.64	23	0.77101
80	13.8	10	28	0.72464
120	13.8	9.1	34	0.65942
180	13.8	9.1	34	0.65942
240	13.8	9.1	34	0.65942

Table: Concentration and % removal of toluene by photo catalysis using Degussa p25 at 60cfm

Time	Inlet(ppm)	Outlet(ppm)	% Removal	C/Co
15	9	7	22	0.63636
30	11	9	18	0.81818
60	11	8.5	22	0.81818
80	11	8	27	0.72727
120	11	7	36	0.63636
180	11.5	7	39	0.63636
240	11	7	36	0.63636

Table: Concentration and % removal of toluene by photo catalysis using Degussa p25 at 60 cfm

Time	Inlet(ppm)	Outlet(ppm)	% Removal	C/Co
15	8.54	7.28	14	0.85246
30	11.17	9.06	19	0.8111
60	11.17	9.59	19	0.85855
80	11.17	9	19	0.80573
120	11.17	7.74	30	0.69293
180	11.17	7.74	30	0.69293
240	11.17	7.74	30	0.69293

Table: Concentration and % removal of toluene by photo catalysis using Degussa p25 at 87 cfm

Time	Inlet(ppm)	Outlet(ppm)	% Removal	C/Co
15	9	7.5	14	0.88235
30	8	6.7	16	0.78824
60	8.2	6.8	17	0.8
80	8.5	6.5	24	0.76471
120	8.5	6	30	0.70588
180	8.5	6	30	0.70588
240	8.5	6	30	0.70588

Table: Concentration and % removal of toluene by photo catalysis using Degussa p25 at 87 cfm

Time	Inlet(ppm)	Outlet(ppm)	% Removal	C/Co
15	9.59	8.65	9	0.90198
30	8.54	7.28	15	0.85246
60	8.54	7.28	15	0.85246
80	8.54	7	18	0.81967
120	8.54	5.9	30	0.69087
180	8.54	5.9	30	0.69087
240	8.54	5.9	30	0.69087

Table: Concentration and % removal of toluene by photo catalysis using Degussa p25 at 117 cfm

Time	Inlet(ppm)	Outlet(ppm)	% Removal	C/Co
15	4.5	4	11	0.80808
30	5	4.4	12	0.88889
60	4.9	4.4	10	0.88889
80	4.9	4	18	0.81633
120	4.9	3.9	20	0.78788
180	5	3.9	22	0.78788
240	5	3.9	22	0.78788

Table: Concentration and % removal of toluene by photo catalysis using Degussa p25 at 117 cfm

Time	Inlet(ppm)	Outlet(ppm)	% Removal	C/Co
15	7.49	7.28	2	0.97196
30	4.86	4.51	7	0.92841
60	4.86	4.51	7	0.92841
80	4.86	4	18	0.82305
120	4.86	3.59	26	0.73868
180	4.86	3.59	26	0.73868
240	4.86	3.59	26	0.73868

Table : Concentration and % removal of xylene by photolysis at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	9	8	0	0.88889
30	13	13	0	1
60	13	13	0	1
80	13	12	8	0.92308
120	13	11.7	10	0.9
180	13	11.7	10	0.9
240	13	11.7	10	0.9

Table: Concentration and % removal of xylene by photolysis at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	27	17.53	0	0.6492593
30	12.87	13.01	0	1.010878
60	14.71	14.71	0	1
80	14.71	13.25	10	0.9
120	14.71	13.29	9	0.903467
180	14.71	13.29	9	0.903467
240	14.71	13.29	9	0.903467

Table: Concentration and % removal of xylene by photolysis at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	9	9	0	1
30	13	13	0	1
60	13	13	0	1
80	13	12.8	2	0.98462
120	13	12.01	7	0.92385
180	13	12.01	7	0.92385
240	13	12.01	7	0.92385

Table: Concentration and % removal of xylene by photolysis at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	14.71	14.71	0	1
30	13.01	13.01	0	1
60	13.01	13.01	0	1
80	13.01	13	0	1
120	13.01	12.45	4	0.9569562
180	13.01	12.45	4	0.9569562
240	13.01	12.45	4	0.9569562

Table: Concentration and % removal of xylene by photolysis at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	9	9	0	1
30	8.5	8.5	0	1
60	8.5	8.5	0	1
80	8.5	8.4	1	0.98823
120	8.5	8.2	3.5	0.96471
180	8.5	8.16	4	0.96
240	8.5	8.16	4	0.96

Table: Concentration and % removal of xylene by photolysis at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	10.19	3.69	0	0.3621197
30	8.92	8.92	0	1
60	8.92	8.92	0	1
80	8.92	8.53	4	0.956228
120	8.92	8.63	3	0.9674888
180	8.92	8.63	3	0.9674888
240	8.92	8.63	3	0.9674888

Table: Concentration and % removal of xylene by photolysis at 117 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	8	8	0	1
30	8	8	0	1
60	8	8	0	1
80	8	8	0	1
120	8	8.2	0	1.025
180	8	7.8	2	0.975
240	8	7.8	2	0.975

Table: Concentration and % removal of xylene by photolysis at 117 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	14.71	7.78	0	0.5288919
30	8.21	8.21	0	1
60	8.21	8.21	0	1
80	8.21	8.2	0	0.998781
120	8.21	8.21	0	1
180	8.21	8.07	1	0.9829476
240	8.21	8.07	1	0.9829476

Table: Concentration and % removal of xylene by photocalysis by using Solgel-TiO_2 at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	13.3	13.3	0	1
30	13.3	11.7	12	0.8797
60	13.3	11.7	12	0.8797
80	13.3	11.5	13	0.86466
120	13.3	11	17	0.82707
180	13.3	11	17	0.82707
240	13.3	11	17	0.82707

Table: Concentration and % removal of xylene by photocalysis by using Solgel-TiO_2 at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	13.3	1.14	0	0.08571
30	13.3	11.88	10	0.89323
60	13.3	11.88	10	0.89323
80	13.3	11.77	11	0.83985
120	13.3	11.17	16	0.83985
180	13.3	11.17	16	0.83985
240	13.3	11.17	16	0.83985

Table : Concentration and % removal of xylene by photocalysis by using Solgel-TiO_2 at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	12	11.5	4	0.82143
30	14	12.5	11	0.89286
60	14	12.5	11	0.89286
80	14	12.5	11	0.89286
120	14	12.5	11	0.89286
180	14	12	14	0.85714
240	14	12	14	0.85714

Table: Concentration and % removal of xylene by photocalysis by using Solgel-TiO_2 at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	6.23	5.3	0	0.850722
30	12.31	11.18	9	0.908205
60	12.31	11.18	9	0.908205
80	12.31	11.09	10	0.9
120	12.31	10.89	12	0.884647
180	12.31	10.89	12	0.884647
240	12.31	10.89	12	0.884647

Table: Concentration and % removal of xylene by photocalysis by using Solgel-TiO_2 at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	12	11.5	3	0.95833
30	10	9	8	0.9
60	10	9	8	0.9
80	10	8.96	10	0.896
120	10	8.9	11	0.89
180	10	8.9	11	0.89
240	10	8.9	11	0.89

Table : Concentration and % removal of xylene by photocalysis by using Solgel-TiO_2 at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	2.7	0.86	0	0.31852
30	9.76	9.06	7	0.92828
60	9.76	9.06	7	0.92828
80	9.76	9	8	0.92213
120	9.76	8.63	12	0.88422
180	9.76	8.63	12	0.88422
240	9.76	8.63	12	0.88422

Table : Concentration and % removal of xylene by photocalysis by using Solgel-TiO_2 at 117 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	9	9.5		1.05556
30	9	8.6	4	0.95556
60	9	8.5	5	0.94444
80	9	8.3	7	0.92222
120	9	8.2	8	0.91111
180	9	8.2	8	0.91111
240	9	8.2	8	0.91111

Table: Concentration and % removal of xylene by photocalysis by using Solgel-TiO_2 at 117 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	13.3	9.76	0	0.73383
30	7.65	7.36	4	0.96209
60	7.65	7.36	4	0.96209
80	7.65	7.2	6	0.94118
120	7.65	7.08	7	0.92549
180	7.65	7.08	7	0.92549
240	7.65	7.08	7	0.92549

Table: Concentration and % removal of xylene by photocalysis by using Clay-TiO_2 at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	14.7	14.7	0	1
30	14.7	12.4	15	0.84354
60	14.7	12.4	15	0.84354
80	14.7	12	18	0.81633
120	14.7	11.3	23	0.76871
180	14.7	11.3	23	0.76871
240	14.7	11.3	23	0.76871

Table: Concentration and % removal of xylene by photocalysis by using Clay-TiO_2 at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	12	11	0	0.91666
30	14.7	11.88	19	0.80816
60	14.7	11.88	19	0.80816
80	14.7	11.55	21	0.78574
120	14.7	11.31	23	0.76938
180	14.7	11.31	23	0.76938
240	14.7	11.31	23	0.76938

Table: Concentration and % removal of xylene by photocalysis by using Clay-TiO_2 at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	6.5	7	0	1.15
30	12	10.5	12.5	0.875
60	12	10.5	12.5	0.875
80	12	10.35	13	0.845
120	12	10	17	0.83333
180	12	9.5	20	0.79167
240	12	9.5	20	0.79167

Table: Concentration and % removal of xylene by photocalysis by using Clay-TiO_2 at 60cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	12	11	0	0.91666
30	12.02	10.61	11	0.88269
60	12.02	10.61	11	0.88269
80	12.02	10.45	13	0.86938
120	12.02	9.76	19	0.81198
180	12.02	9.76	19	0.81193
240	12.02	9.76	19	0.81193

Table: Concentration and % removal of xylene by photocalysis by using Clay-TiO_2 at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	8	9	0	1.125
30	8	7.5	6	0.9375
60	8	7.5	6	0.9375
80	8	7.25	9	0.90625
120	8	7.1	12	0.8875
180	8	7.1	11	0.8875
240	8	7.1	11	0.8875

Table: Concentration and % removal of xylene by photocalysis by using Clay-TiO_2 at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	9	8	0	0.88888
30	10.47	9.34	11	0.89207
60	10.47	9.34	11	0.89207
80	10.47	9.23	12	0.88154
120	10.47	8.63	18	0.82425
180	10.47	8.63	18	0.82425
240	10.47	8.63	18	0.82425

Table: Concentration and % removal of xylene by photocalysis by using Clay-TiO_2 at 117 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	7	7.5		1.07143
30	7	6.8	3	0.97143
60	7	6.8	3	0.97143
80	7	6.8	3	0.97143
120	7	6.7	4.5	0.95714
180	7	6.5	7	0.92857
240	7	6.5	7	0.92857

Table: Concentration and % removal of xylene by photocalysis by using Clay-TiO_2 at 117 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	5	4.5		0.9
30	6.94	6.8	2	0.97982
60	6.94	6.8	2	0.97982
80	6.94	6.5	6	0.93659
120	6.94	6.5	6	0.81700
180	6.94	6.5	6	0.81700
240	6.94	6.5	6	0.81700

Table: Concentration and % removal of xylene by photocalysis by using Degussa p25 at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	13.5	13.5	0	1
30	13	11.2	14	0.86154
60	13	11.2	14	0.86154
80	13	10.2	21	0.78462
120	13	10	23	0.76923
180	13	10	23	0.76923
240	13	10	23	0.76923

Table: Concentration and % removal of xylene by photocalysis by using Degussa p25 at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	11.7	11	5	0.94017
30	11.7	10.5	10	0.89744
60	11.7	10.5	10	0.89744
80	11.7	10	15	0.8547
120	11.7	9.2	21	0.78632
180	11.7	9.2	21	0.78632
240	11.7	9.2	21	0.78632

Table: Concentration and % removal of xylene by photocalysis by using Degussa p25 at60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	11	11	0	1
30	11	9.5	13	0.83828
60	11	9.5	13	0.86364
80	11	10	9	0.90909
120	11	9	18	0.81818
180	11	8.5	22	0.77273
240	11	8.5	22	0.77273

Table: Concentration and % removal of xylene by photocalysis by using Degussa p25 at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	9.06	0.58	0	0.06402
30	10.89	9.9	9	0.90909
60	10.89	10	8	0.91827
80	10.89	8.99	17	0.82553
120	10.89	8.92	18	0.8191
180	10.89	8.92	18	0.8191
240	10.89	9	17	0.82645

Table: Concentration and % removal of xylene by photocalysis by using Degussa p25 at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	6.5	6.4	1.5	0.98462
30	6.5	5.8	11	0.89231
60	6.5	5.8	11	0.89231
80	6.5	5.9	9	0.90769
120	6.5	5.6	13	0.86154
180	6.5	5.4	17	0.83077
240	6.5	5.4	17	0.83077

Table: Concentration and % removal of xylene by photocalysis by using Degussa p25 at 25 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	6.94	3.97	0	0.57205
30	6.94	6.52	6	0.93948
60	6.94	6.37	8	0.91787
80	6.94	6.22	10	0.89625
120	6.94	6.09	12	0.87752
180	6.94	5.95	14	0.85735
240	6.94	6.09	12	0.87752

Table: Concentration and % removal of xylene by photocalysis by using Degussa p25 at 117 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	6.5	6.2	4	0.91176
30	6.8	6.3	7	0.92647
60	6.8	6.3	7	0.92647
80	6.8	6.2	8	0.91176
120	6.8	6.3	7	0.92647
180	6.8	6.2	8	0.91176
240	6.8	6.1	10	0.89706

Table: Concentration and % removal of xylene by photocalysis by using Degussa p25 at 117 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	%Removal	C/Co
15	4.8	4.9	0	1.02083
30	5.1	4.8	5	0.94118
60	5.24	4.96	5	0.94656
80	5.24	4.7	10	0.89695
120	5.24	4.67	10	0.89122
180	5.24	4.67	10	0.89122
240	5.24	4.67	10	0.89122

Table: Concentration and % removal of toluene with relative humidity (14% RH) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	10	9.6	4
60	10	9.6	4
120	10	9.1	9
180	10	9.1	9
240	10	9.1	9

Table: Concentration and % removal of toluene with relative humidity (14% RH) at 87cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	8.35	8.07	3
60	8.35	8.07	3
120	8.35	7.9	5
180	8.35	7.9	5
240	8.35	7.9	5

Table: Concentration and % removal of toluene with relative humidity (17% RH) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	9	8.46	6
60	9	8.46	6
120	9	8	11
180	9	8	11
240	9	8	11

Table: Concentration and % removal of toluene with relative humidity (17% RH) at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	7.8	7.5	3
60	7.8	7.5	3
120	7.8	7.3	6
180	7.8	7.3	6
240	7.8	7.3	6

Table: Concentration and % removal of toluene with relative humidity (20% RH) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	9.2	8.45	8
60	9.2	8.45	8
120	9.2	7.9	14
180	9.2	7.9	14
240	9.2	7.9	14

Table: Concentration and % removal of toluene with relative humidity (14% RH) at 87cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	7.9	7.5	5
60	7.9	7.5	5
120	7.9	7.3	7.5
180	7.9	7.3	7.5
240	7.9	7.3	7.5

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Table: Concentration and % removal of xylene with relative humidity (14% RH) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	12.5	12.12	3
60	12.5	12.12	3
120	12.5	11.75	6
180	12.5	11.75	6
240	12.5	11.75	6

Table: Concentration and % removal of xylene with relative humidity (14% RH) at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
15	0	0	0
30	8.8	8.6	2
60	8.8	8.6	2
120	8.8	8.4	4.5
180	8.8	8.4	4.5
240	8.8	8.4	4.5

Table: Concentration and % removal of xylene with relative humidity (17% RH) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	11.8	11.21	6
60	11.8	11.21	6
120	11.8	10.9	7.6
180	11.8	10.9	7.6
240	11.8	10.9	7.6

Table: Concentration and % removal of xylene with relative humidity (17% RH) at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	8	7.65	4
60	8	7.65	4
120	8	7.5	6
180	8	7.5	6
240	8	7.5	6

Table: Concentration and % removal of xylene with relative humidity (20% RH) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	12	11.18	7
60	12	11.18	7
120	12	10.8	10
180	12	10.8	10
240	12	10.8	10

Table: Concentration and % removal of xylene with relative humidity (20% RH) at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	8.2	7.79	5
60	8.2	7.79	5
120	8.2	7.5	8
180	8.2	7.5	8
240	8.2	7.5	8

Table: Concentration and % removal of toluene with light intensity(0.077mw/cm^2) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	9.07	9.07	0
60	9.07	9.07	0
120	9.07	8.54	6
180	9.07	8.54	6
240	9.07	8.54	6

Table: Concentration and % removal of toluene with light intensity(0.077mw/cm^2) at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
15	0	0	0
30	8.54	8.54	0
60	7.48	8.54	0
120	7.48	7.48	0
180	7.48	7.28	2.6
240	7.48	7.28	2.6

Table: Concentration and % removal of toluene with light intensity (1.44mw/cm^2) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	10	10	0
60	10	10	0
120	10	9.1	9
180	10	9.1	9
240	10	9.1	9

Table: Concentration and % removal of toluene with light intensity (1.44mw/cm^2) at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	8.35	8.35	0
60	8.35	8.35	0
120	8.35	7.9	5
180	8.35	7.9	5
240	8.35	7.9	5

Table: Concentration and % removal of xylene with light intensity (0.072mw/cm^2) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
15	0	0	0
30	13.01	13.01	0
60	13.01	13.01	0
120	13.01	12.45	4
180	13.01	12.45	4
240	13.01	12.45	4

Table: Concentration and % removal of xylene with light intensity (0.072mw/cm^2) at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
15	0	0	0
30	8.92	8.92	0
60	8.92	8.92	0
120	8.92	8.63	3
180	8.92	8.63	3
240	8.92	8.63	3

Table: Concentration and % removal of xylene with light intensity (1.44mw/cm^2) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	12.5	12.5	0
60	12.5	12.5	0
120	12.5	11.75	6
180	12.5	11.75	6
240	12.5	11.75	6

Table: Concentration and % removal of xylene with light intensity (1.44mw/cm^2) at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	8.8	8.8	0
60	8.8	8.8	0
120	8.8	8.4	4.5
180	8.8	8.4	4.5
240	8.8	8.4	4.5

Table: Concentration and % removal of toluene with Degussa p25(using dip-coating) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	12.7	11	13
30	12	9.6	20
60	12	9.6	20
120	12	8.16	32
180	12	8.16	32
240	12	8.16	32

Table: Concentration and % removal of toluene with Degussa p25(using dip-coating) at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	12	9.6	17
60	12	9.6	17
120	12	8.16	25
180	12	8.16	25
240	12	8.16	25

Table: Concentration and % removal of toluene with N-doped TiO_2 (using dip-coating) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	13	12	7
30	11.5	10.1	12
60	11.5	10.1	12
120	11.5	9.2	20
180	11.5	9.2	20
240	11.5	9.2	20

Table: Concentration and % removal of toluene with N-doped TiO_2 (using dip-coating) at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	10	9.5	5
30	8.5	7.9	7
60	8.5	7.9	7
120	8.5	7.4	13
180	8.5	7.4	13
240	8.5	7.4	13

Table: Concentration and % removal of toluene with Bi_2O_3 (using dip-coating) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	10	8	20
30	12	9.96	17
60	12	9.96	17
120	12	8.64	28
180	12	8.64	28
240	12	8.64	28

Table: Concentration and % removal of toluene with Bi_2O_3 (using dip-coating) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	7	7	0
30	8	6.92	13.5
60	8	6.92	13.5
120	8	6.32	21
180	8	6.32	21
240	8	6.32	21

Table: Concentration and % removal of xylene with Degussa p25(using dip-coating) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	11	9.2	16
60	11	9.2	16
120	11	8.2	25
180	11	8.2	25
240	11	8.2	25

Table: Concentration and % removal of xylene with Degussa p25 (using dip-coating) at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	6.9	6.1	12
60	6.9	6.1	12
120	6.9	5.5	20
180	6.9	5.5	20
240	6.9	5.5	20

Table: Concentration and % removal of xylene with N-doped TiO_2 (using dip-coating) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	10.5	9.6	9
60	10.5	9.6	9
120	10.5	9.1	13
180	10.5	9.1	13
240	10.5	9.1	13

Table: Concentration and % removal of xylene with N-doped TiO_2(using dip-coating) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	20
30	6	5.6	6
60	6	5.6	6
120	6	5.4	10
180	6	5.4	10
240	6	5.4	10

Table: Concentration and % removal of xylene with Bi_2O_3 (using dip-coating) at 60 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	10	8.9	15
60	10	8.9	15
120	10	8.2	21
180	10	8.2	21
240	10	8.2	21

Table: Concentration and % removal of xylene with Bi_2O_3(using dip-coating) at 87 cfm

Time(min)	Inlet(ppm)	Outlet(ppm)	% Removal
0	0	0	0
30	6	5.52	11
60	6	5.52	11
120	6	5.16	16
180	6	5.16	16
240	6	5.16	16

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